

STUDY OF ANODIC OXIDE FILM OF  
ALUMINIUM FOR  
AUTOMOTIVE AND ENVIRONMENTAL  
APPLICATIONS.

*A thesis submitted  
in partial fulfilment of the requirements  
for the degree of  
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*by*  
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*to the  
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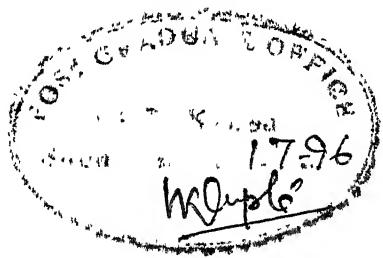
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## CERTIFICATE

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## ABSTRACT

The excellent corrosion resistance of pure aluminium is largely due to its affinity for oxygen, resulting in the production of a very tenacious thin (of the order of nano meter) oxide film which covers the surface as soon as a freshly cut piece of the metal is exposed to atmosphere.

This oxide coating is of great industrial significance involving use of aluminium in various applications. It is of course, particularly the anodic oxide film on aluminium which is vastly used currently as decorative and corrosion resistance coating on aluminium wares. However great many other possibilities of the phenomenon exist for useful applications. Two important aspects of these films are mainly their use as abrasive resistance coating on automobile moving parts such as pistons and cylinders or newer possibilities of using as adsorbent coating for gases or ions.

In the present work, these two aspects have been considered for studies. As a result the variation of micro hardnesses of anodized aluminium with various anodization parameters and aging of coating have been investigated. There is excess presence of fluoride ions in water in many parts of India and the World. Therefore, an attempt has been made to study the chemisorption of anodic aluminium films.

## INTRODUCTION

### 1.1 PROPERTIES OF ALUMINIUM

Aluminium is a strongly electronegative metal and possesses a strong affinity for oxygen, this is apparent from high heat of formation of its oxide.

Its other important properties on which the application of aluminium is based are its low density of approximately  $2.7\text{gm/cm}^3$  the high mechanical strength achieved by suitable alloying and heat treatments and relatively high corrosion resistance of the pure metal. Other valuable properties include its high thermal and electrical conductances, good reflectivity, its high ductility and resultant low working cost, its magnetic neutrality, high scrap-value, and the nonpoisonous and colourless nature of its corrosion products. These facilitates its use in the chemical and food processing industries. Still further valuable features are obtained by various treatments of the metal. These will be considered when the applications of aluminium and its finishes are considered.

In its pure state, aluminium is however, a relatively soft metal with yield strength of only  $34.5 \text{ N/mm}^2$  and a tensile strength of  $90 \text{ N/mm}^2$ . However development of a wide range of alloys have resulted to of alloys, very varied strengths and ductility. Consequently this has led to many of its applications today ranging from thin foil material in the packaging industry, drink containers, electrical conductors, structural parts in building industry and high strength materials for automobile, aircraft & armoured vehicles.

The metal in its pure state has a relatively high corrosion resistance and needs less protection than most metals. On the other hand, the commercial metal and its high strength alloys containing heavy metals such as copper, zinc or nickel are more sensitive to corrosion and need protective surface treatments. The development of satisfactory protective finishes for these metals has been, therefore, of very great importance.

## 1.2 THE OXIDE FILM

When a freshly formed aluminium metal surface is exposed to the atmosphere, it is immediately covered with a thin film of oxide, and this oxide film quickly re-forms when damaged. An important and beneficial feature of this oxide film is that its molecular volume is stoichiometrically 1.5 times that of the metal used up in oxidation. This means that the oxide film is under compressive stress, and will not only cover the metal continuously, but can cope with a certain amount of substrate

deformation without rupturing. It is to this protective surface layer that the aluminium industry owes its existence.

The structure of this low temperature, air formed film is assumed to be amorphous, with the outer surface being a hydrated aluminium oxide. At higher temperatures (above  $450^0\text{C}$ ) crystalline  $\gamma\text{-Al}_2\text{O}_3$  is formed, and then, in the molten state,  $\alpha\text{-Al}_2\text{O}_3$  can occur. Transformation from  $\gamma$ -phase to  $\alpha$ -alumina has been reported to occur around  $500^0\text{C}$  ( Rai et al.)<sup>32</sup>.

The kinetics of oxide growth on pure aluminium are complex. The currently accepted mechanism has been described recently by (Wefers.<sup>1</sup>). At ambient temperatures a limiting oxide film thickness of 2 to 3 nm will be produced within one day; thermal oxidation is controlled by diffusion of aluminium and oxygen ions at temperatures up to  $\sim 400^0\text{C}$  and in this temperature range, asymptotically decaying rate law is observed.<sup>1</sup> However, when temperature is raised towards and above  $450^0\text{C}$ , the exponential oxidation rate changes to a linear relationship between weight gain and time. This change in mechanism represents crystallisation to  $\gamma\text{- Al}_2\text{O}_3$ , which will disrupt the continuity of the film. At temperatures above  $500^0\text{C}$ , it has been reported<sup>2,1</sup> that the preparation of the sheet. i.e both metallurgical and surface roughness features, can alter the oxidation kinetics.

TABLE -1.1

## THICKNESS OF OXIDE COATINGS ON ALUMINIUM

Natural oxide film on pure Al (formed at temps. above 300° C)	1 - 3 nm
Natural oxide film on pure Al (formed at temps. above 300° C)	up to 30 nm
Natural oxide film on Al- Mg alloy (formed at temps. above 300° C)	up to 3,000 nm depends on Mg content
Normal chemical oxide coating (e.g. M.V.V.Alrok, etc.)	2,500 - 5,000 nm
Normal barrier layer anodizing	250 - 750 nm
Normal protective anodic coating (e.g sulphuric acid anodizing)	5,000 - 30,000 nm
Hard anodic coatings (e.g for engineering purposes)	25,000 - 150,000 nm

Magnesium is the major alloying element incorporated within the oxide film. At temperatures above 340° C,<sup>3</sup> magnesium diffuses from the bulk of the alloy and, even at levels less than 50 ppm of magnesium, there is a competitive oxidation reaction between magnesium diffusion outwards and oxygen diffusion inwards. At higher levels of magnesium content (up to 4 %), a duplex film of Aluminium oxide close to the metal, and an outer layer of MgO, results. These oxide films will thicken until the bulk magnesium levels is depleted. Typical weight gain curve for

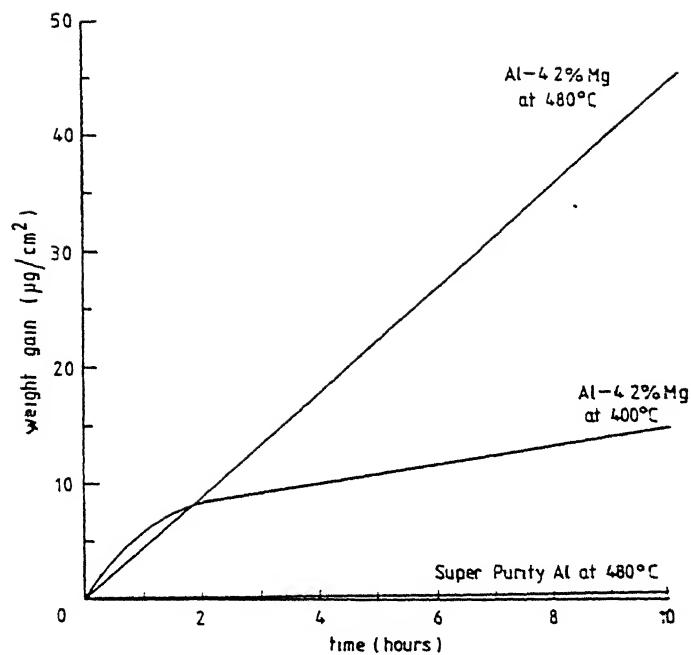
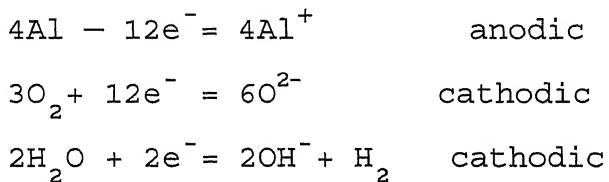


Fig 1.1 Comparision of weight gain curve for oxidation under dry conditions.<sup>2</sup>

Al-4.2 % Mg, as compared to super-purity aluminium, are shown in Fig 1.1.<sup>2</sup> The current status of oxidation of aluminium-magnesium alloys is summarized by wefers<sup>1</sup> and Field et al.<sup>5</sup> in table 1.1 which shows the thickness of typical natural oxide coatings in comparison with chemical and anodic oxidation coatings.

Break down of the oxide film can result from mechanical rupture, or from chemical attack by anions such as chloride ions. In most cases repair is instantaneous and, depending on the moisture content of environment, can either be accompanied by the oxygen reduction reaction or the hydrogen evolution reaction shown below.



In the first cathodic reaction aluminium oxide results, where as in the second, hydroxide is formed.

There is growing evidence that flaws pre-exist in the oxide film, and can act as nucleation sites for film breakdown. Information has been gained both from electrochemical studies<sup>6,7</sup> and transmission electron microscopy.<sup>8</sup> It is proposed that, in solution, flaws are continually being developed and repassivated. The presence of aggressive ions hinders the repassivation step, allowing pits to nucleate. Electrochemical

noise generated prior to pit initiation provides strong evidence for this type of process. However, even with the existence of flaws, the aggressive ions would still have to penetrate the flaw bases. This could be by the formation of short - lived complex ions or by the development of islands of salts e.g  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ , followed by current less dissolution.<sup>9</sup> Alternatively , the local pH in the flaw may become sufficiently low to effectively defilm the base of the flaw and expose the aluminium. The latter mechanism is favored at present. The result of film breakdown is corrosion and this is considered in the next section.

### 1.3 CORROSION OF ALUMINIUM

While aluminium and its alloys generally have good corrosion resistance, localized forms of corrosion can occur, and it is important to understand the factors contributing to these forms of corrosion.

Corrosion may be defined as the reaction between a metal and its immediate environment, which can be natural or chemical in origin. The most recognizable form of corrosion is, perhaps, the rusting of iron. All metals react with natural environments but the extent to which this happens can vary. For noble metals like gold the amount is insignificant whereas for iron it is considerable. Aluminium is no exception but, fortunately, it has the propensity of self passivation and for many applications corrosion is not a problem.

#### 1.4 FACTOR CONTRIBUTING TO CORROSION

There are two main factors which influence the general corrosion behavior of aluminium, one is the type and aggressiveness of the environment and the second is that of its chemical and metallurgical structure. Environments can vary from outdoors atmospheres to media such as soils, waters building materials, food and chemicals etc. Outdoor atmospheres are usually classified as either rural, industrial or marine depending on there location. In rural atmospheres the degree of natural pollution is usually low, but industrial and marine environments are more aggressive, due to presence of sulphates and chlorides respectively. Soils, waters and building materials vary in aggressiveness depending on such properties as composition, chemical activity, degree of aeration and electrical conductivity, chemical environments usually have unique compositions and their corrosion effects can be fairly accurately determined.

Pure aluminium displays the highest corrosion resistance, but as purity decreases and alloying elements are added this resistance decreases<sup>10</sup> copper lowers the resistance more than other elements, while magnesium has the least effect. The influence of the main alloying elements and impurities on the corrosion resistance of aluminium is summarized below in Table -1.1

TABLE - 2.1<sup>11</sup>

General effect of major alloying elements on the corrosion resistance of aluminium.

ELEMENT	EFFECT			
	Marked	Moderate	Slit	V.Slit
Copper .....	*			
Magnesium .....				*
Zinc .....				*
Manganese .....				*
Silicon .....		*		
Chromium .....				*
Zirconium .....				*
Titanium .....				*
Iron + Silicon .....	*			

#### 1.5 TYPES OF CORROSION

Aluminium displays a number of different corrosion modes, sometimes within the same alloy. The most common form, in natural environments, is that of pitting.<sup>12</sup> This mode is a random process initiating from various sites on the metal surface where the air formed oxide film is defective. In practice this means that the unprotected aluminium surface becomes roughened and less reflective with the development of numerous localised pits. Fortunately for aluminium, the pits eventually stifle and

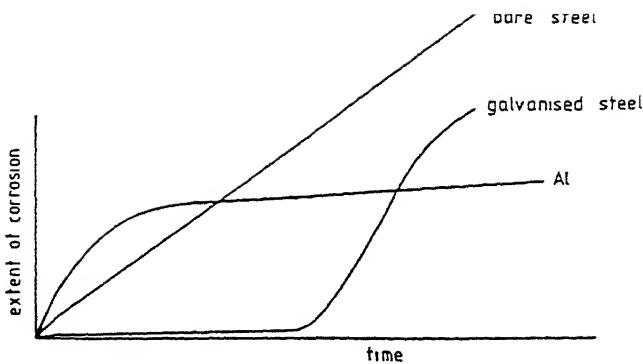


Fig 1.2 Threshold corrosion behaviour of aluminium compared with that of bare galvanised steel.<sup>34</sup>

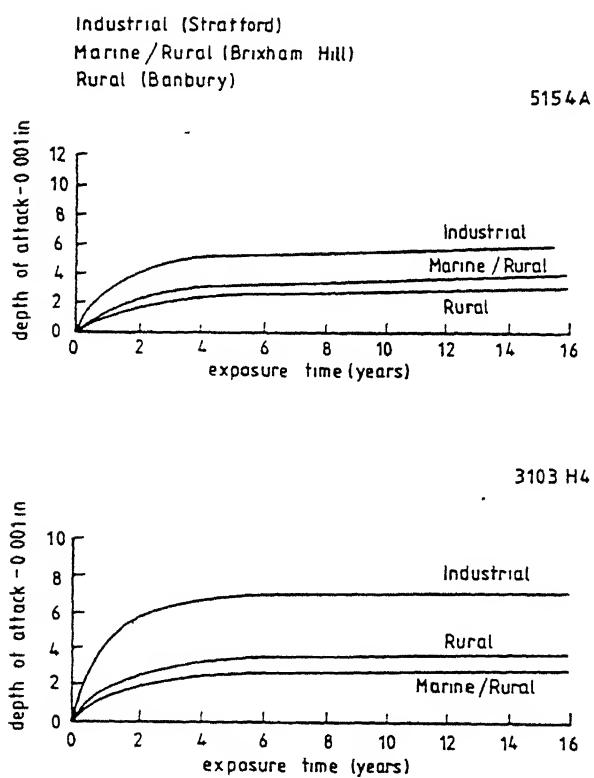


Fig 1.3 Corrosion-time curves for the sheet alloys 5154A and 3103.<sup>34</sup>

in consequence the amount of corrosion which occurs reaches a limiting or "threshold" value. this behavior is well established and can be safely predicted and referred to in design considerations. A typical corrosion time curve, in comparison with bare and galvanized steel, is shown in Fig.1.2 Some examples of the corrosion - time relationship for some of aluminium alloys are given in Fig.1.3 .

#### 1.6 PROTECTION OF ALUMINIUM

For many applications aluminium requires no protection and everyday examples of its excellent resistance can be seen as roofing, siding, automotive parts & bodies, ships superstructures etc. This high resistance is due to the tenacious air formed oxide film which develops at its surface, and the ability of the film to re-form when damaged. However, to ensure maximum corrosion resistance under the more stringent environmental uses, when some of the previously mentioned types of corrosion may occur, the following factors are important.

1. Correct choice of alloy in relation to service condition, with special regard to purity in composition and strict material control.
2. Careful control during fabrication.
3. Correct design in service to avoid such features as crevices or encatchments for moisture, and galvanic effects.
4. Use of the best protective system.

Protection may take the form of cathodic protection systems, sealants, inhibitors metal spraying and applied coatings or finishes.

The manner in which anodic oxidation differs essentially from other industrial electrolytic processes will be apparent from the following three examples all using dilute sulphuric acid, say 10% by volume, as the electrolyte.

If the electrodes are made of platinum or any other metal that does not dissolve at the anode a positive electrode, oxygen gas is liberated at the anode and hydrogen gas at the cathode. No metal is dissolved in the acid. If the anode is made of copper it will dissolve in the acid and will be redeposited on the cathode. This is the basis of many metal electrodeposition processes. In commercial production with soluble metal anodes little or no gas is evolved at the anode and cathode.

When the anode is aluminium, in commercial practice, is either aluminium or lead. When current is passed through the aluminium anode does not dissolve away like copper, nor is oxygen evolved in quantity. Instead, most of oxygen that would have been liberated combines with the aluminium to form a layer of porous aluminium oxide, hydrogen is liberated at the cathode.

The amount of aluminium oxide formed is directly proportional to the current density and time i.e to quantity of electric current used. The progress of the formation of the anodic coating depends upon the chemical composition of the anodizing electrolyte and the chosen condition of electrolysis.

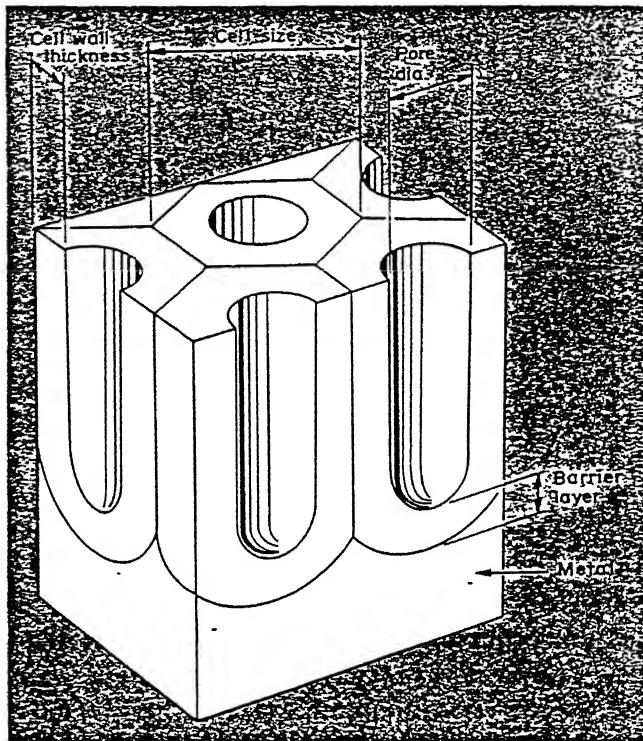


Fig 1.4 Microstructure of anodic Film.<sup>35</sup>

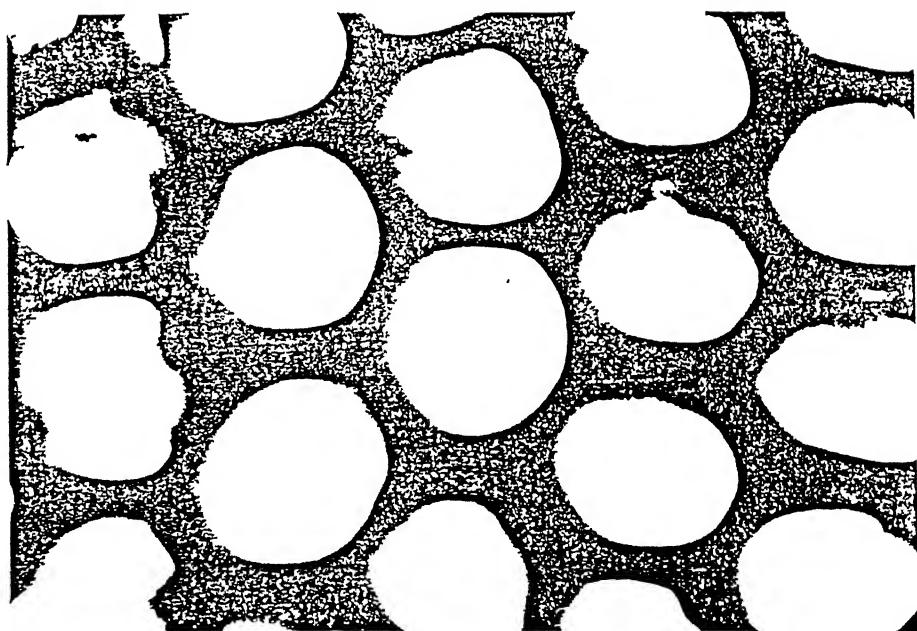


Fig 1.5 Transmission electron micrograph of an aluminium foil

25  $\mu\text{m}$  thinned by  $\text{H}_3\text{PO}_4$  solution ( $\text{M} \times 200,000$ ); anodizing voltage 45 V (Rai & et al).<sup>32</sup>

Some anodizing electrolytes have little or no solvent action on the oxide coating so that the process soon ceases, leaving a thin film usually referred to as a barrier-layer type coating, the thickness of the barrier layer is solely governed by the applied voltage and approximates to  $1/700\mu\text{m}$  per volt. This type of coating is typically produced in solutions of borates, boric acid or tartrates.

If the electrolyte has some solvent action, on newly formed alumina layer, then a porous film is formed and the oxidation process can continue leading to production of relatively thick films, as for example in sulphuric acid. Eventually the rate of film formation is balanced by the rate of solvent attack, but this stage of the process is avoided in the commercial practice.

This structure of the porous type of anodic oxide coating is shown diagrammatically in fig 1.4 and can be seen comprise hexagonal columns each with a central pore which reaches down to a thin compact barrier layer which is continuously formed and transformed into the porous form during the process.

The diameter of the pores and thickness of the barriers layer for any given electrolyte and temperature are proportional to the applied voltage. Thus by varying the anodizing conditions it is possible to alter the physical properties of the coating, such as the hardness, abrasion resistance and the density<sup>14</sup>.

From the forgoing it will be appreciated that anodizing is a conversion process so that the appearance and other properties are completely dependent up on the composition of the aluminium and its surface condition. Anodizing, therefore, differs fundamentally from processes such as electroplating where a layer of metal is applied over the basis metal surface.

After anodizing, the film is usually sealed by a hydrate on process to minimize the initial porosity. For some special applications physical sealing with an organic materials such as oil is desirable. Colouring by immersion in dye solutions is carried out after anodizing but before sealing.

With aluminium alloys the constituents are differently affected by the anodizing process, and in turn influence the appearance and structure of the coating.

The properties of the coatings can also be modified by chemical additions to the electrolyte.

#### 1.8 ALUMINIUM SELECTION FOR ANODIZING

When selecting material for work that is eventually to be anodized the manufacturer choice will be guided by the type of finish that is required. In some cases the mechanical properties of the aluminium will be of prime importance, e.g. aircraft & automobile components subjects to stress in service. Here the choice will be limited and the appearance becomes of secondary importance.

Where resistance to atmospheric corrosion is the prime requisite it is often possible to select alloys giving coatings that combine good protection and an attractive appearance.

Many application of anodizing are mainly decorative and here the choice of alloy is most extensive, although for the production of very bright films, comparable with bright chromium plating, alloys of special high purity must be used.

Apart from the differences in the appearance of anodic film on different alloys, other variations can be introduce by mechanical chemical pretreatment of the metal before anodizing. Indeed it is not unusual deliberately to modify the metal surface so as to obtain the best possible matching among different alloys, for example, sheet metal extrusions and castings.

In addition to the effects of varying alloy composition it is necessary to take note of any heat treatment that may be required to ensure the correct mechanical properties of the metal. Variations in heat treatment can modify the appearance of the coating. Therefore as basic guide for anodizing, the grades should be selected as according to Table 1.2 .

TABLE 1.2  
ANODIZING CHARACTERISTICS OF WROUGHT ALUMINIUM <sup>15</sup>

		Protective	Colour	Bright	Hard
1080A	- 0	E	E	V-E	E
	- H 8	E	E	V-E	E
1050	- O	E	E	V	E
	- H 8	E	E	V	E
1200	- 0	V	V	G	E
	- H 4	V	V	G	E
	- H 8	V	V	G	E
2011	- TD	F	F (D)	U	G
	- TF	F	F (D)	U	G
2014	- TB	F	F (D)	U	G
	- TF	F	F (D)	U	G
2024	- TB	F	F (D)	U	G
	- TB	F	F (D)	U	G
2618A	- TF	F	F	U	F
3103	- 0	G	G	P-F	G
	- H4	G	G	P-F	G
	- H8	G	G	P-F	G
3105	- 0	G	G	P-F	G
	- H4	G	G	P-F	G
	- H8	G	G	P-F	G
5005	- 0	E	E	E	E
	- H4	E	E	E	E

	- H8	E	E	E	E
5083	- 0	V	V	G	E
	- H2	V	V	G	E
	- H4	V	V	G	E
5154A	- 0	V	V	G	E
	- H2	V	V	G	E
	- H4	V	V	G	E
6061	- TB	G	G	F	V
	- TF	G	G	F	V
6063	- TB	V	V	G-V	E
	- TF	V	V	G-V	E
6082	- TB	G	G	F	G-V
	- TF	G	G	F	G-V
7020	- TB	F	F	†	G
	- TF	F	F	†	G
7075	- TF	F	F	†	F

E = Excellent

V = Very good

G = Good

F = Fair

P = Poor

D = Dark colour only

U = Unsuitable

\* compared on the basis of a 50µm film thickness.

† Variable response, depending on actual composition and heat treatment.

Properties of anodized aluminium depend on a combination of the following factors

- (a) Grades of aluminium alloy.
- (b) Pre-treatment processes.
- (c) The anodizing processes.
- (d) Post anodizing processes.

A very wide range of chemical solutions have been used or proposed as anodizing electrolytes. Most electrolytes are acidic, but some alkaline solutions have been investigated. The greatest tonnage of anodizing is produced in sulphuric acid-based solutions but other acids are used on a commercial scale in order to obtain special types of coatings.

(A) SULPHURIC ACID

On all alloys except those containing insoluble constituents anodizing in sulphuric acid produces semi-transparent colourless films in thickness up to about  $35\mu\text{m}$ . When properly processed and sealed those coatings are suitable for both decorative and corrosion resistant applications. The appearance of the coating is considerably influenced by the original surface finish of the aluminium.

The so-called "bright anodizing" is achieved by selecting alloys based on high-purity (99.7% +) aluminium or alloys based on it, followed by a brightening process and then anodizing in sulphuric acid.

At low temperatures, e.g.  $-5^{\circ}\text{C}$  to  $5^{\circ}\text{C}$  the sulphuric acid process gives very hard coatings (Known as "hard anodizing") and are widely employed in the engineering industry.

The sulphuric acid electrolyte can also be modified to produce films that will withstand a certain amount of forming without disrupting the film. This type of process is used for the anodizing (and colouring if required) of continuous strip.

#### (B) OXALIC ACID

Solutions of this acid tend to produce translucent hard yellowish films that have been used for architectural applications and also, in Japan, for cook ware. The abrasion resistance is almost double that of a conventional sulphuric acid-process coating.<sup>33</sup> This process is one of the earliest "integral colour process" to achieve universal recognition.

#### (C) ANODIZING CURRENT SUPPLY:-

Most anodizing process operates with direct current which is usually supplied by a rectifier. Modern rectifiers are constructed with silicon diodes and when operated from a three-phase supply are arranged to give a "hexaphase" output which minimizes ripple a figure below 5% ripple full load is achievable. Excessive ripple is the result of too large a residual A C component in the D.C out put and can give rise to the formation of faults in anodic coating.

In our experiments we have used I.C regulated D.C power supply N.P.S 60/2. Control of the anodizing process should aim at constant voltage. The resistance of the film increases as anodizing proceeds, so the current density decreases slightly during the process. For general purposes the current density should be in the range of 1.0-1.5 amp/dm<sup>2</sup>, but it can be as low as 0.5 or high as 3.5 amp /dm<sup>2</sup>. The lower current densities are for thin, transparent films which are clearer than films of equal thicknesses produced at higher current densities, the higher current densities are used in continuous anodizing. High current densities tend to counter balance the high dissolution rates in strong electrolytes.

#### (D) RELATION BETWEEN FILM THICKNESS WITH TIME ANODIC CURRENT<sup>16</sup>

The factors affecting the duration of anodizing are the thickness of film that is required, the alloy and the current density used. For pure aluminium, as a first approximation

$$\text{Thickness} = \frac{\text{current density (amp/dm}^2 \text{). time (min)}}{3} .$$

i.e at 1.5 amp/dm<sup>2</sup> the film grows at 0.5  $\mu\text{m}/\text{min}$  . The rough guide must not supplant physical methods of measuring film thickness. Considerable variation occur with extremes in processing conditions and with different alloys.

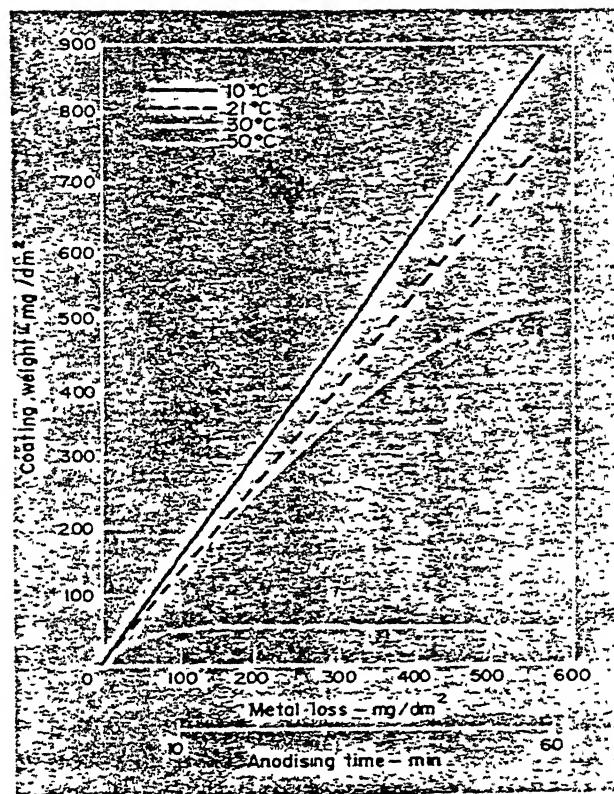


Fig 1.6 Influence of Electrolyte on coating weight/metal loss relationship (15% sulphuric acid, 19 amp/ft<sup>2</sup>).<sup>31</sup>

## (E) ELECTROLYTE TEMPERATURE

For ordinary processes the bath temperature ranges from about 18 to 25°C for most purposes 20°C is appropriate. The film produced in cold electrolytes are harder and less absorbent than those produced in warm electrolytes. The process known as " hard anodizing " (using refrigerated electrolytes). Close temperature control is important, because the current density and the rate at which the film is dissolved by the solution markedly with temperature. These factors in turn affect the properties of the film and in particular the " blooming " of the film, which in some forms may not occur until a long period after anodizing. High temperatures tend to give powdery films. Automatic control (for example by thermostat) within +/- 1°C is essential for consistent results.

## 1.10 MODIFICATION OF ANODIZED SURFACE :

Following are the important modifications of anodized surfaces. These are the protection of film from atmospheric effects and imparting of colour to the anodized surfaces for the decorative look. These are discussed below.

- (a) Protection Of Anodic Film
- (b) Colouring Of Anodic Film
- (c) Ruby Films
- (d) Opaque Coatings

#### 1.10.1 PROTECTION OF ANODIC FILM :-

Cleaning of anodized aluminium is very important if the finish is to be preserved. Fox-Williams and Watts believe that dirt which settles on the surface holds moisture and forms corrosion if allowed to remain,<sup>18</sup> and it is certain that anodized finishes on accessible surfaces, e.g. shop fronts, window frames, etc, have an appreciably longer life than surfaces which are cleaned infrequently. This effect is so pronounced that areas which are frequently cleaned may be anodized with thinner coatings e.g., 15µm, without suffering undue deterioration.

Hubner and Schiltknecht<sup>19</sup> give the following formula for "Lumiclean", a mild polishing and cleaning composition for anodized aluminium which is used once or twice a year for cleaning anodized material.

Bentonite	6.0%
Liquid paraffin	8.0%
Slaked lime	10.0%
Wetting agent	0.5%
Oil or winter green	0.05%
Water	75.45%

To prepare this compound, the bentonite is mixed into four fifths of the water and allowed to stand with periodic stirring for about 5 days. The slaked lime is stirred into a paste with the remainder of the water and this and the other ingredients are added to the bentonite paste with stirring for 10-20 minutes. The cleaning compound is wiped on to the surface with a clean cloth.

Much work on the cleaning of anodized aluminium has been carried out in Germany in recent years,<sup>20</sup> and special cleaning formulations have been developed.<sup>21, 22</sup> While the benefit of suitable abrasive cleaning treatment is recognized, the high cost and labour involved in such cleaning methods has led workers to seek alternatives. These take the form of acid based cleaners using acids such as tartaric acid, citric acid, acetic acid, lactic acid, certain esters of phosphoric acid and in some cases nitric acid. Stronger acids such as hydro fluric acid, hydrochloric acid, sulphuric acid and phosphoric acid have been shown to cause serious film damage.<sup>22</sup> A test, in which the anodized aluminium is immersed in the cleaners for 8 hrs at 20-22°C, has been developed,<sup>20</sup> and after drying no visible colour change, no surface dulling, no loss of anodic film thickness and no change in admittance value on the tested samples are acceptable. The formulations developed are said to have equal cleaning effect to abrasive cleaning in most circumstances.

Regular cleaning is essential if the finish of anodized aluminium is to be preserved over the years, since deterioration of the anodic oxide coating can occur mainly as a result of grime deposition and subsequent attack by moisture on the anodized surface, permitting attack to proceed and thereby damaging the anodic oxide coating which can not be renewed.

The anodized aluminium should be washed down with warm water containing a suitable wetting agent or with a mild soap

solution. Fiber brushes may be used to loosen attached grime but the use of emery, sand paper, steel wool or other abrasive materials, and acid or alkaline cleaners should not be permitted as they damage the anodic oxide coating. It is essential to rinse thoroughly after cleaning using copious applications of clean water, particularly where crevices are present. Where greasy deposits are concerned, cleaning may be by means of a soft cloth dipped in white spirit. After cleaning, the anodized aluminium may be treated with good quality wax polish.

Since emulsion cleaners or proprietary chemical agents may attack the anodic oxide coating, they should never be used except in consultation with companies specializing in the cleaning of anodized aluminium.

In considering the behavior of anodized aluminium installations in principally industrial urban atmosphere, such as in Paris, Darnault<sup>22.1</sup> has distinguished four stages. In the first deposits of grime can be readily removed by washing with a sponge and water containing a wetting agent, which is the case where maintenance is carried out more than once in a year. In the second stage the grime deposits yield less readily and require a very fine abrasive powder for restoring the surface, which is the case when cleaning is carried out less than once a year. In the third stage where the surfaces are not cleaned for four or five years a more vigorous action is required where an abrasive pad must be applied. The fourth stage is reached when surface has

received no maintenance for a period of about ten years when the grime has become so ingrained in the surface that the original appearance can only be restored by the mechanical cleaning appliances.

#### 1.10.2 COLOURING OF ANODIC FILM

While natural anodic finishes are attractive in themselves, the range of decorative applications is extended by colouring the film, practically any variation in depth and hue can be obtained, as well as multi colour effects.

The main characteristics determining the suitability for colouring are the

- (1) Thickness of the coating
- (2) Absorptive power and
- (3) Its natural colour.

On appropriate grades of aluminium the sulphuric acid process gives semi-transparent and colourless coating ideal for dyeing to pastel shades or full, rich tones for maximum fastness to light, resistance to weathering and depth of colour, a  $25\mu\text{m}$  or thicker coating is essential. Where thin coating are dyed the colour fastness is reduced(e.g with bright anodized aluminium for artificial jewellery).

The opaque off-white coatings of the chromic acid process are ideal for mellow pastel shades, the colour fastness is adequate for general interior work provided suitable dye stuffs used. However this is inadequate for external exposure.

The oxalic acid process, produces effects similar to those with sulphuric acid. Incidentally shade is modified if the original oxalic acid film has a golden colour. In all the anodizing processes films with maximum retention of colouring matter are obtained by anodizing at the higher limits of temperature, time and acid concentration. Other properties required in the anodic film, however, often modify these conditions.

To achieve uniformity of colour the anodic film must be of even thickness and produced in conditions avoiding local variations in temperature or acid concentration.

#### (A) TREATMENT BEFORE COLOURING

After anodizing, work should be given two rinses in clean cold running water. Special care is needed to carry over of acid into the dye bath. Dirt grease and finger marks must be scrupulously avoided, as they cause undyed patches in the finished work.

There should be minimum delay between rinsing and dying, to avoid lowering of the absorptive capacity of the film for dyestuff. However when, stopping-off compounds must be applied for multi-coloured effects, the rinsing should be immediately followed by a thorough drying in warm air. Incomplete drying will result in a patchy finish. Dried film may

stored for long periods, but with some loss in absorptive capacity.

The work should be wet when introduced into the dye bath, otherwise patchiness may result.

Selection of Colouring Agent<sup>17</sup> :

The table below list the Organic Dyestuff For aluminium having anodized film of about 25  $\mu\text{m}$ .

Colour	Dyestuff	concentration	pH	temperature	Time
Yellow	aluminium	3	5.5	60	20-30
	Yellow 3GL				
Dark blue	aluminium	5	5.5	60	20 30
	Blue G				
Turquoise	Aluminium	12	5.0	60	20-30
Blue	Turquoise PLW				
Red	Aluminium Red	5	5.5	60	20-30
	B3LW				
Black	Aluminium Deep	8	4.5	60	30-40

(C) COLOURING PROCEDURE WITH ORGANIC DYES

After weighing, the dye is made into a smooth paste with cold water and then dissolved in boiling water before it is put into the dyebath. Complete solution is essential. Softened water is very desirable in all dye baths, Particularly when maximum colour fastness is required. Mains water in some cases contains appreciable quantities of calcium and magnesium which form insoluble compounds with dyestuff, thus leading to a loss of expensive dyes.

#### (D) COLOURING WITH INORGANIC PIGMENTS

Many of the general operating recommendations given for organic dyes also apply to inorganic pigments. In these processes insoluble coloured inorganic substances are deposited within pores of films and in general colour produced are more stable to light and heat than organic colours.

Gold shades are obtained by immersion in 8-10 gm/lit of ferric ammonium oxalate at a temperature of 40-50°C and pH of 5.0 - 5.5. The yellow colour result due to iron oxide depositing from the complex salt within the anodic film. Due to photo chemical reaction during use, the iron hydroxide precipitates form the above solution. It is therefore essential to resolve the hydroxide by adding 5 gm/litre of oxalic acid at 60°C after settling for two hours. The pH is adjusted as desired.

#### (E) PIGMENT COLOURING BY DOUBLE DECOMPOSITION :

One of important examples is gold, bronze and black shade obtained by cobalt acetate potassium permangnate method.

Two solution are made:

- (a) 30gm/litre potassium permangnate.
- (b) 5gm/litre cobalt acetate.

The freshly anodized work is put into the cobalt acetate solution at 50°C for 2 minutes, quickly rinsed and transferred to the potassium permangnate solution at 30°C for 2

minutes. A gold-brown cobalt/manganese oxide mixture is precipitated in the coating. By repeating the operation the depth of colour is increased and with a specially absorbent thick coating it is possible to achieve a black finish. The operations are carried out under manual control and skilled operators are necessary to produce consistent colour matching. The light to medium bronze shades given by this process can be closely matched by one of the electrolytic colouring solutions described in the next section.

#### (F) ELECTROLYTIC COLOURING

In general terms the process consists of submitting the freshly anodized work to electrolysis in a heavy metal salt solution using A.C, D.C special wave forms. The anodic coating acts as the cathode while the anode is usually made of stainlees steel. At the cathode, metal is deposited in a finally divided form at the bottom of the pores of the coating. Depending on the metal in the electrolyte a variety of colours can be developed, their depth increasing with the time of treatment. For example, solution of nickel, tin or cobalt or mixtures of them give colours ranging from very light yellowish colour through bronze to black. The light fastness is outstanding. Copper solutions give pink-maroon black colours but their corrosion resistance and light fastness are less reliable. Dilute solutions of silver salts give gold bronze coloures.

### 1.10.3 RUBY FILMS

The ruby films <sup>23</sup> are produced in a two steps of anodizing process, in which high purity aluminium is first anodized for 80 minutes at  $1.0 \text{ A/dm}^2$  in a 15% (vol) sulfuric acid electrolyte. Metal ions are particularly chromium ions, are the adsorbed within the film by single or double dipping treatments in a range of metal salt solution in Table 1.3. Finally the metal pigmented films are anodized to form alpha alumina films in a molten salt mixture of sodium bisulphate and ammonium bisulphate (1:1.15 mole) at  $170^\circ\text{C}$  for 10 minutes at  $1.0 \text{ A/dm}^2$ . It can be seen from table 1.3 that only the chromium incorporating films had a reddish violet colour and also emitted a red fluorescence through some other metal ions gave bright or dark violet fluorescence. The use of ammonium chromate gave the best result and a 10g/L solution used at  $70^\circ\text{C}$  with an immersion time of 30 minutes is recommended.

Table 1.3 Colour and Fluorescence of alumina films obtained by two step anode oxidation<sup>24</sup>

Absorbed Inorganic Compounds	Two- step Alumina films.	
	Colour	Fluorescence
Single dipping process		
$(\text{NH}_4)_2\text{CrO}_4$	light green	deep red
$\text{Fe}_2(\text{C}_2\text{O}_4)_3\text{Na}_2\text{C}_2\text{O}_4$	yellowish light grey	dark violet.
$\text{Fe}_2(\text{C}_2\text{O}_4)_3\text{K}_2\text{C}_2\text{O}_4$	grey	dark violet.

$\text{Fe}_2(\text{C}_2\text{O}_4)_3(\text{NH}_4)_2\text{C}_2\text{O}_4$	grey	dark violet.
Alternate dipping process		
$\text{Pb}(\text{Ac})_2 + \text{K}_2\text{Cr}_2\text{O}_7$	light reddish violet	red
$\text{K}_2\text{Cr}_2\text{O}_7 + \text{AgNO}_3$	light reddish violet	red
$\text{AgNO}_3 + \text{K}_2\text{Cr}_2\text{O}_7$	light reddish violet	red
$\text{Ni}(\text{Ac})_2 + (\text{NH}_4)_2\text{S}$	yellowish light grey	dark violet
$\text{CdSO}_4 + (\text{NH}_4)_2\text{S}$	light grey	bright violet
$\text{AgNO}_3 + (\text{NH}_4)_2\text{S}$	khaki	dark violet
$\text{Co}(\text{Ac})_2 + \text{Na}_2\text{S}$	light grey	bright violet
$\text{AgNO}_3 + \text{Na}_2\text{S}$	yellowish light grey	dark violet
$\text{CuSO}_4 + \text{Na}_3\text{PO}_4$	light grey	bright violet
$\text{Pb}(\text{Ac})_2 + \text{Na}_3\text{PO}_4$	light grey	bright violet
$\text{Pb}(\text{Ac})_2 + \text{Na}_2\text{SO}_4$	light grey	bright violet
$\text{Co}(\text{Ac})_2 + \text{KMnO}_4$	light grey	dark violet

#### 1.10.4 OPAQUE COATINGS

The most important of these is the metal process developed by Schenk<sup>25</sup> in use mainly in Switzerland, which employs an oxalic acid solution containing salts of thallium, zirconium or titanium. These salts hydrolyse in the coating, the hydroxides producing a milky, opaque, non-metallic appearance which somewhat resembles porcelain enamel. The bath is operated at 2-3 A/dm<sup>2</sup> d.c. and 120 volts. The operating time is 20 - 40 minutes, and solution is kept at 50 - 70°C. The pH of the solution is critical and must be kept at 1.6 to 3.0.

The corrosion resistance is claimed to be superior to that of sulphuric acid coatings, and the coating can be dried satisfactorily, especially to pastel shades. The most wrought alloys containing less than 2% copper, and casting alloys containing less than 1% Mn, 1% Fe, 1% Ni, 2% Cu, and 8% Zn or Mg are suitable for the treatment by the Ematal process.

In a more recent improvement of the Ematal process by Contrayes A.G.<sup>26</sup> It has been proposed to add cobalt acetate to the electrolyte mixture containing boric acid, citric acid and oxalic acids with potassium titanium oxalate. This is also a high voltage process and the coating is said to be extra ordinarily abrasion resistant. There is a corrected manner for preparing the electrolyte, the cobalt acetate being added from a prepared solution only when the bath is in use and activated. Two electrolytes are suggested, one suitable for alloys of the low copper content and the other for use when the copper content of the alloy is high. (See Table 1.4)

Table 1.4  
Improved Ematal process<sup>26</sup>

	Alloys Low in Cu	Alloys with Cu
Potassium Titanium Oxalate (g/l)	45	50.55
Boric acid	12	14
Citric acid	0.8	1.5
Oxalic acid	1.5	1.8

Cobalt Acetate	1.2	0.5 - 1.0
Temperature (°C)	58 - 60	35 - 38
Voltage	110	110

In a later version the electrolyte contains potassium - titanium oxalate, cobalt acetate, nickel acetate, nickel sulphates and 0.3 - 0.6 ml/litre sulphuric acid. The coating formed is said to be electronically conductive.<sup>27</sup>

Similar opaque coating can also be obtained in a mixture containing.<sup>28</sup> Chromic acid 3% (wt), Boric acid 0.1 - 0.2% (wtf) at 0.3 A/dm<sup>2</sup>, 40 - 60 volts, 40 - 55°C and in the mixed electrolytes

		I	II
Cromic acid	( % wt )	10	5
Oxalic acid	( % wt )	2	0.5
Boric acid	( % wt )		0.2-0.5
Phosphoric acid	( % wt )	2	
Water		Balance	Balance
Current density (amp/sq ft)		5 - 8	8 - 10
Voltage		20 - 30	25 - 40
Temperature °C		30 - 50	30 - 50

The French BF<sub>4</sub> anodizing process, which is also based on a mixture of chromic, oxalic and boric acid is used at 42 - 48°C, 40- 45 Volts and 0.81 A/dm<sup>2</sup> and is reported to be employed in the French industry<sup>29</sup>. The opaque coating obtained are built up to 20 μm in 60 minutes and may be dyed. Super imposed A.C. may also be used to obtain a white or grey-yellow film.

## MATERIALS & PROCESSES

### 2.1 ABSTRACTS :-

This chapter deals with materials and equipments used, process adopted for obtaining anodic oxide surface of aluminium and various method of characterizing the anodized surfaces.

### 2.2 MATERIAL USED :-

Important materials used in the present investigations were

- (a) Aluminium.
- (b) Oxalic acid.
- (c) Distilled water.
- (d) caustic soda.
- (e) Abrasive paper. etc

#### (A) ALUMINIUM SHEET :-

Commercial grade aluminium sheet of 3mm and 1.5mm was used for sample preparation. The purity of aluminium was obtained by electron probe micro analyzer analysis.

#### (B) OXALIC ACID :-

Oxalic acid  $(COOH)_2 \cdot 2H_2O$  of laboratory reagent grade supplied by s.d Fine-Chemicals Limited Boisar401501, used as aqueous solution in the concentration of 0.16 M. The contents of oxalic acid were as follows.

Oxalic acid (COOH) <sub>2</sub> .2H <sub>2</sub> O	99.5%
Maximum limit of impurities	0.1%
Chloride (Cl)	0.0005%
Sulphate (SO <sub>4</sub> )	0.02%
Heavy metals and iron (Fe)	0.005%

(C) DISTILLED WATER :-

Water used for making electrolyte was single stage distilled.

(d) SODIUM HYDROXIDE PELLETS: -

Aqueous solution of sodium hydroxide was used for chemical cleaning of aluminium samples' surface. It was of analytical grade. Manufactured by,

Ranbaxy Laboratories Limited

S.A.S, Nagar

Punjab, India.

Content of NaOH used was as follows.

Minimum assay	98.00%
Insoluble matter	0.01%
Carbonate (Na <sub>2</sub> CO <sub>3</sub> )	1.0%
Chloride (Cl)	0.0005%
Nitrate (NO <sub>3</sub> )	0.0005%
Phosphate (PO <sub>4</sub> )	0.001%
Silicate (SiO <sub>2</sub> )	0.01%
Sulphate (SO <sub>4</sub> )	0.003%
Aluminium (Al)	0.001%
Ammonium (NH <sub>4</sub> )	0.0005%
Arsenic (As)	0.0004%

Calcium (Ca)	0.002%
Iron (Fe)	0.001%
Lead (Pb)	0.0005%
Nickel (Ni)	0.001%
Zinc (Zn)	0.001%

(e) ABRASIVE PAPER :-

To remove the formed oxide layer of the aluminium samples' surfaces and to polish it the different grades of abrasive papers (viz. 300, 600, 0/1, 0/2, 0/3, & 0/4, grades) were used.

Manufacturers of abrasive papers is as follows.

300 & 600 grade was made by,

Jhon Oakey & Mohan Limited.

Mohan Nager (U.P), India.

0/1, was made by ,

DEE Kay

Grand Wel, India.

0/2, 0/3, 0/4 , were made by

S I A

1600

SIANORB

SWITZER LAND

or

John Oakey & Sons Ltd.

Wellington, England .

### 2.3 EQUIPMENTS USED :-

Main equipment used were as follows :-

- (A) D.C Power supply
- (B) Thermometer
- (C) Electric furnace
- (D) Electronic balance
- (E) Air blower
- (F) Vacuum deposition machine
- (G) Scanning electron microscope (S E M)
- (H) Electron probe micro analyzer (E P M A)
- (I) X- ray diffraction machine
- (J) Micro hardness tester.

(A) D.C power supply :-

I.C regulated D.C power supply NPS 60/6 voltage range 0 to 60 volts, current range 0 to 2 ampere.

Manufactured by Networks Private Ltd.  
113/121 Swarup Nagar  
Kanpur (U.P)

(B) Thermometer:-

Mercury thermometer of range  $-10^{\circ}\text{C}$  to  $10^{\circ}\text{C}$  manufactured by HICKS India Ltd, was used to monitor the temperature of the electrolyte during anodizing process.

(C) Electric furnace :-

Box type, automatic temperature controlled electric furnace was used for annealing the sample.

(D) Air blower:-

While polishing sample were being dried by air blower after each wash.

(E) Electronic balance:-

For weighing the oxalic acid and NaOH for making aqueous solution of desired concentration. An electronic balance brand name "Afcoset" range 0.01mg to 100 gm was used.

(F) Vacuum deposition machine:-

To improve the brightness of anodized samples, silver coating was done by vacuum deposition machine.

(G) Scanning electron microscope (SEM) :-

This was used to study the nature of anodized surface and to measure the thickness of oxide film.

(H) Electron Probe Micro analyzer (EPMA) :-

EPMA analysis was done to find out the chemical constituents of virgin aluminium and anodized surface.

(I) X-Ray Diffraction:--

X-ray diffraction was done to study the crystallography of anodized surface.

(J) Micro-Hardness Tester :-

This equipment was used to, measure the micro hardness of the virgin and anodized surface.

## 2.4 ANODIZATION OF SAMPLE

### 1 SAMPLE PREPARATION.

### 2 ANODIZATION .

#### 2.4.1 SAMPLE PREPARATION :-

For the preparation of samples following processes were followed.

- (1) Machining of sample
- (2) Initial cleaning
- (3) Removal of natural oxide
- (4) Polishing of sample
- (5) Annealing of sample
- (6) Chemical wash
- (7) Elemental analysis
- (8) Preparation of electrolyte

#### (1) MACHINING OF SAMPLE :-

The plate type samples of sizes 3mmx5mmx30mm and 3mmx30mmx30mm were machined from commercial aluminium plate. Indentation due to gripping of the jaw on the machining lath was avoided by introducing plastic or polymer separator between the plate and the jaw surface. After machining the burs and sharp edges were cleaned nicely by filling.

#### (2) INITIAL CLEANING:-

After machining oil grease and adhered dirt were

removed by cotton . Then oil grease and dirt adhered with samples were washed off properly by detergent powder (good quality) and washed properly by the tap water.

(3) REMOVAL OF NATURAL OXIDE LAYER :-

By filing and rubbing with 300 and 600 grade abrasive papers the naturally formed oxide layer was removed properly from the surface of samples.

(4) POLISHING OF SAMPLE :-

After removal of natural layer of oxide the samples were mechanically polished through 0/1 to 0/4 grades of abrasive paper. Samples were washed and dried to avoid carry over of abrasive grits from one stage to another stage of polishing.

After polishing up to 0/4 grades abrasive paper, it was polished up to mirror finish on a low speed (300& 600 rpm) polishing wheel with very fine alumina grits.

(5) ANNEALING :-

Machining of samples produced stresses and distortions due to cold working. Hence to remove stresses and distortions samples were annealed at  $300^{\circ}\text{C}$  for 3hrs in an electric furnace and followed by furnace cooling (at the rate of 5 to  $6^{\circ}\text{C}/\text{hr}$ ).

(6) CHEMICAL WASH :-

Annealing caused thermal oxidation of aluminium surface along with partially carburised grease particles. These may lead to poor adhesion of oxide film. Hence, care was taken to clean the substrates. Therefore, chemical cleaning of the sample was further carried out in NaOH solution (5%by wt.) as mentioned earlier. After chemical wash samples were further washed in tap

water. After complete removal of caustic soda content from samples, the samples were washed in distilled water and then dried properly without finger touch on the surface of samples. After complete drying samples were stored in a clean desicator for storage. Then samples were ready for anodization.

Bare handed, handling of caustic soda solution is hazardous for skin. Hence good quality hand gloves were used while chemical wash.

#### (7) ELEMENTAL ANALYSIS BY EPMA :-

The chemical composition of samples was found out using EPMA ( JEOL Analysis ) test.

#### (8) PREPARATION OF ELECTROLYTE :-

Electrolyte of concentration 0.16 M was made. Calculations for wt, of Oxalic acid and volume of distilled water were as follows. For getting 1 molar concentration electrolyte, 63.035gm. Oxalic acid was require to mix with one liter distilled water. Therefore, for getting electrolyte of 0.16M concentration, 20.16 gm Oxalic acid was mixed with one liter of distilled water.

#### 2.4.2 ANODIZATION PROCESS :-

The oxide layer was formed over the aluminium samples by anodization in an electrolytic cell (Fig2.1). Using electrolyte of 0.16M. the electrodes were connected to D.C power supply through crocodile clips and immersed in electrolyte producing parallel electrode configuration hanging down vertically. The details of configurations is shown below in (Fig.2.1). The precautions were taken to prevent the contact point between

## I.C. Regulated D.C. Power Supply

Range 0-60 Volts, 0-2 Amps.

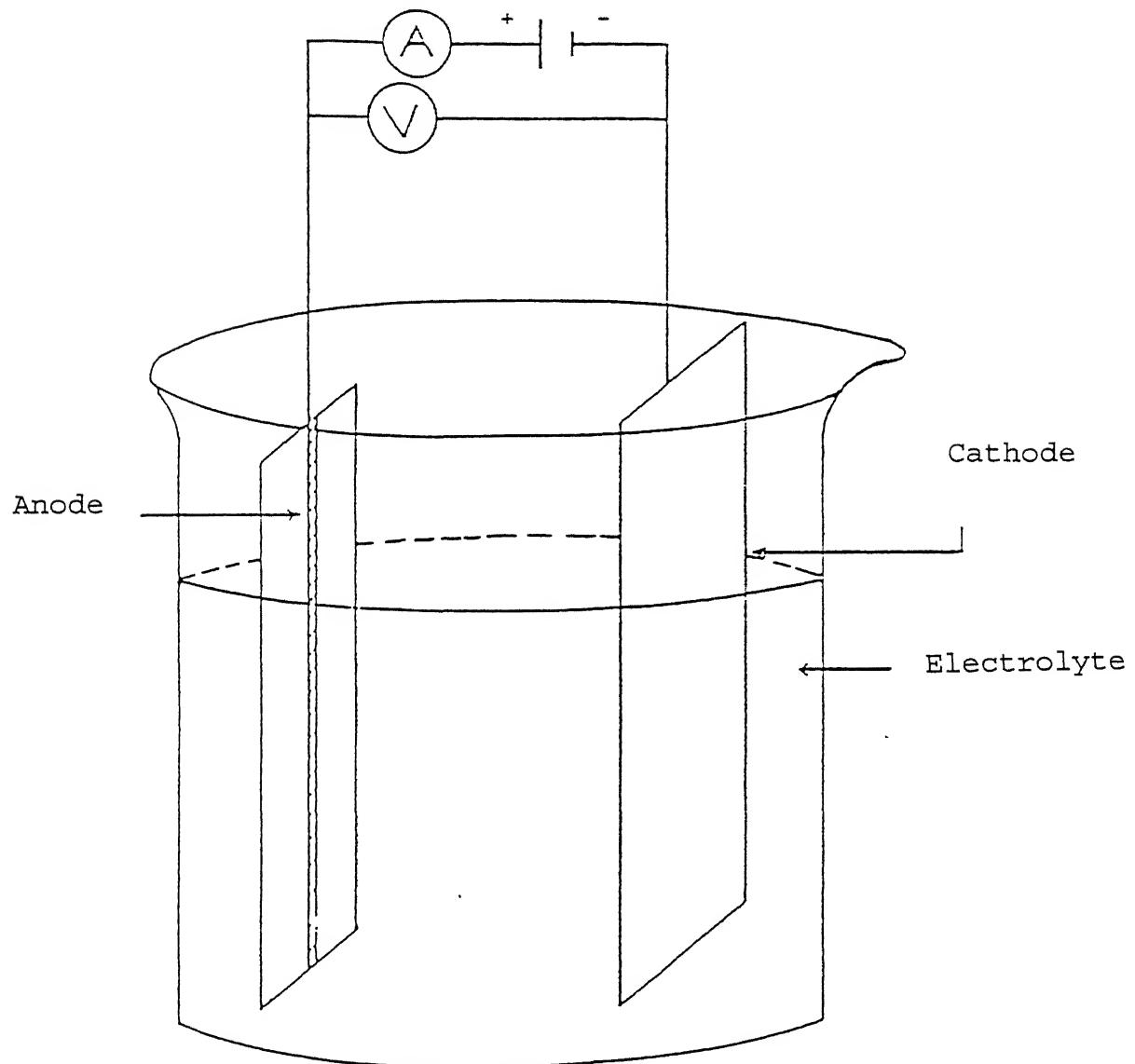


Fig 2.1 Schematic diagram og anodization set-up.

electrodes and crocodile clips being in contact with electrolytes which otherwise would have produced excess corrosion at the site also the edge of the electrodes were coated with polymeric lacquer before introducing in to electrolyte in order to avoid undesirable excess electrochemical reaction on the edge sites. Anodizing parameters such as electrolytic concentration, current density, anodizing voltage and electrode separation were optimized to obtain anodic film with least effort.

#### 2.4.3 WASHING AND DRYING :-

After anodization for different conditions of voltage, current, distance between electrodes etc, the anodized samples were cleaned with distilled water and dried with an air blower. Dried and cleand anodized samples were stored in a desicator for further characterizations. While washing and drying precautions were taken to avoid finger touch on the anodized surfaces.

#### 2.5 CHARACTERIZATION OF ANODIZED SURFACE

Characterization of anodised surface consist of following study.

- (a) Electron metalography
- (b) X-ray Diffraction
- (c) Micro Hardness measurement
- (d) Active surface area determination of florid ions.

##### 2.5.1 ELECTRON METALOGRAPHY:-

To see the surface structure and to measure the thickness of anodic film formed on the anodized surface electron

scanning microscopic study was carried out for getting %age concentration of Al, Cu, Fe, Mg, & Si, EPMA, tests were performed.

#### 2.5.2 X-RAY DIFFRACTION :-

X-ray diffraction pattern of anodized surface was found out for the crystallography study.

X-ray source used was = Cu  $K_{\alpha}$ .

Scanning speed = 12

Chart speed = 12 cm / min .

Count per mint = 5 K

#### 2.5.3 MICRO-HARDNESS:-

The micro hardness tests were performed virgin and of anodized samples at different conditions of anodizing and aging to see the improvements in hardness, wear resistance , corrosion resistance etc.

## RESULTS AND DISCUSSIONS

The results of experimental observations such as chemical composition (of virgin and anodized aluminium), electron metallography of oxide coating, micro hardness variation of anodized aluminium with anodizing conditions, artificial aging and chemisorption process of  $F^-$  ions on anodized surface are reported in this chapter.

## 3.1 ELECTRON METALLOGRAPHY :

Electron metallography consisted of following two types of observations.

- (a) The imaging of surface topography by Scanning Electron Microscopy (SEM) and
- (b) Electron probe micro analyzer (EPMA) analysis of virgin and anodized samples.

The micro structures of both the virgin and anodized surfaces of flat aluminium sheets anodized for 5,10 and 20 minutes are shown in Fig 3.1 to Fig 3.4 respectively. The Fig 3.5 is taken from edge of the anodized sheet and shows the relative contrast of virgin and anodized aluminium layer.

The results of electron probe micro analysis of virgin and anodized (for 10 minutes) samples are shown in Table 3.1 and Table 3.2 respectively and difference in chemical contents of anodized and virgin sample is shown in Table 3.3 . It is found that elements like Mg, Fe, and Cu deplete from the aluminium

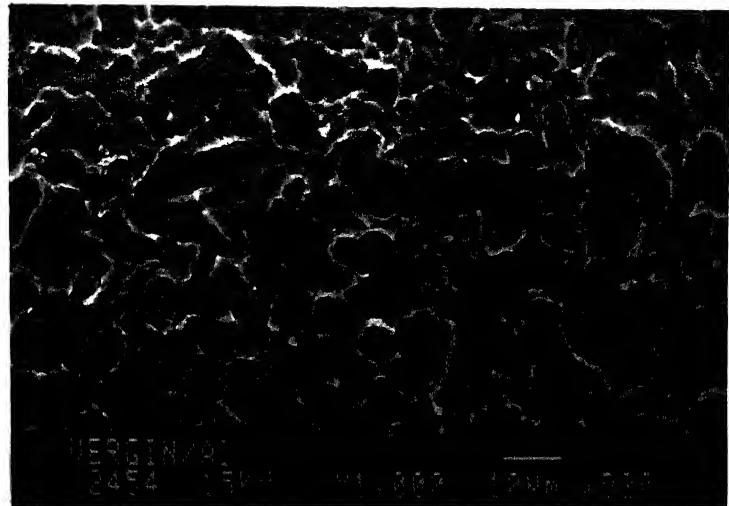


Fig 3.1 Microstructure of Virgin Sample.

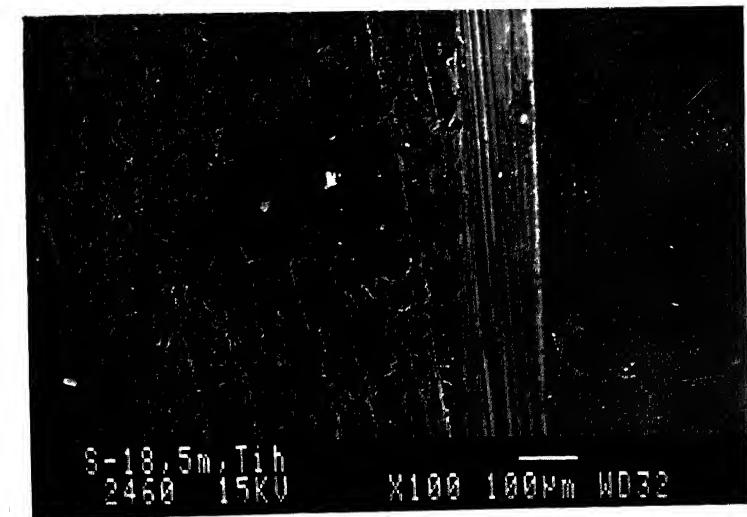


Fig 3.5 Shows the relative contrast of virgin and anodized aluminium layer

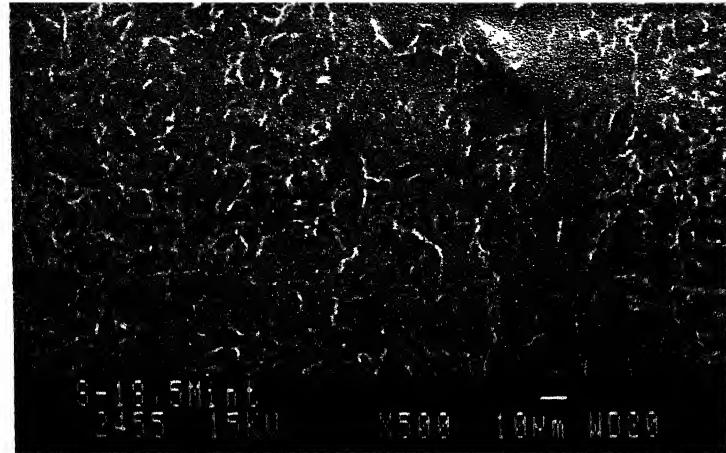


Fig 3.2 Microstructure of sample anodized for 5 mins.

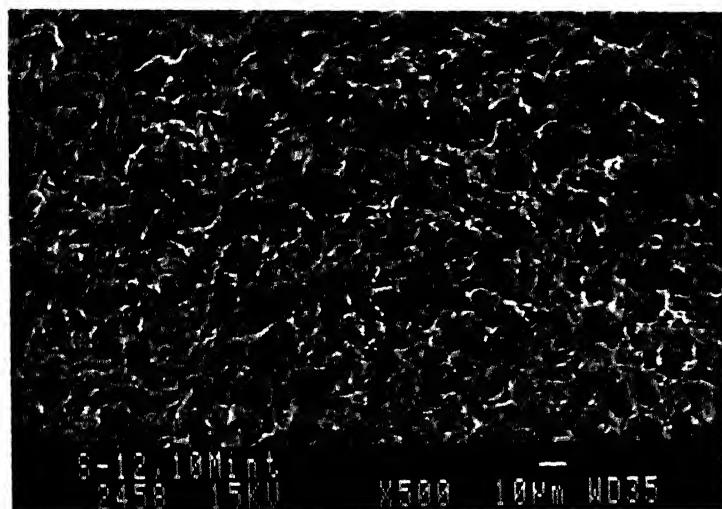


Fig 3.3 Microstructure of sample anodized for 10 mins.



Fig 3.4 Microstructure of sample anodized for 20 mins.

during anodizing operation. The elements seem to pass into electrolyte due to their more electropositive nature. Silicon however seems to remain with anodic coating after being oxidized at the anode.

### 3.2 X-RAY DIFFRACTION ANALYSIS.

The X-ray diffraction patterns of an anodized sample is shown in Fig 3.6 and important values are presented in Table 3.4. The peaks (a), (b), (c) and (d) in this pattern are due to pure aluminium (f.c.c,  $a=4.050 \text{ \AA}^0$ ) and their Miller indices are (311), (220), (200), (111) respectively. The peaks shown in Fig 3.6 (e) marked as 1, 2, 3 & 4 seem to appear due to anodized coating. However these could not be indexed due to non availability of crystallographic data.

### 3.3 MICRO HARDNESS MEASUREMENT:

The micro hardness of virgin and samples anodized for 5, 10, 15 and 20 minutes are presented in Table 3.5 to 3.32. The micro hardness of anodized samples have been studied under two following groups.

- (a) The micro hardness variation due to anodizing time (at fixed voltage).
- (b) The micro hardness variation due to aging.

The anodizing current due to changes in temperatures of electrolytes varies with time. Thus anodizing current was taken as average over the duration of experiment. The variation of anodizing current due to change in temperature is shown in Tables 3.5, 3.12, 3.19 & 3.25.

MICROHARDNESS OF ANODIZED SAM. FOR 5min

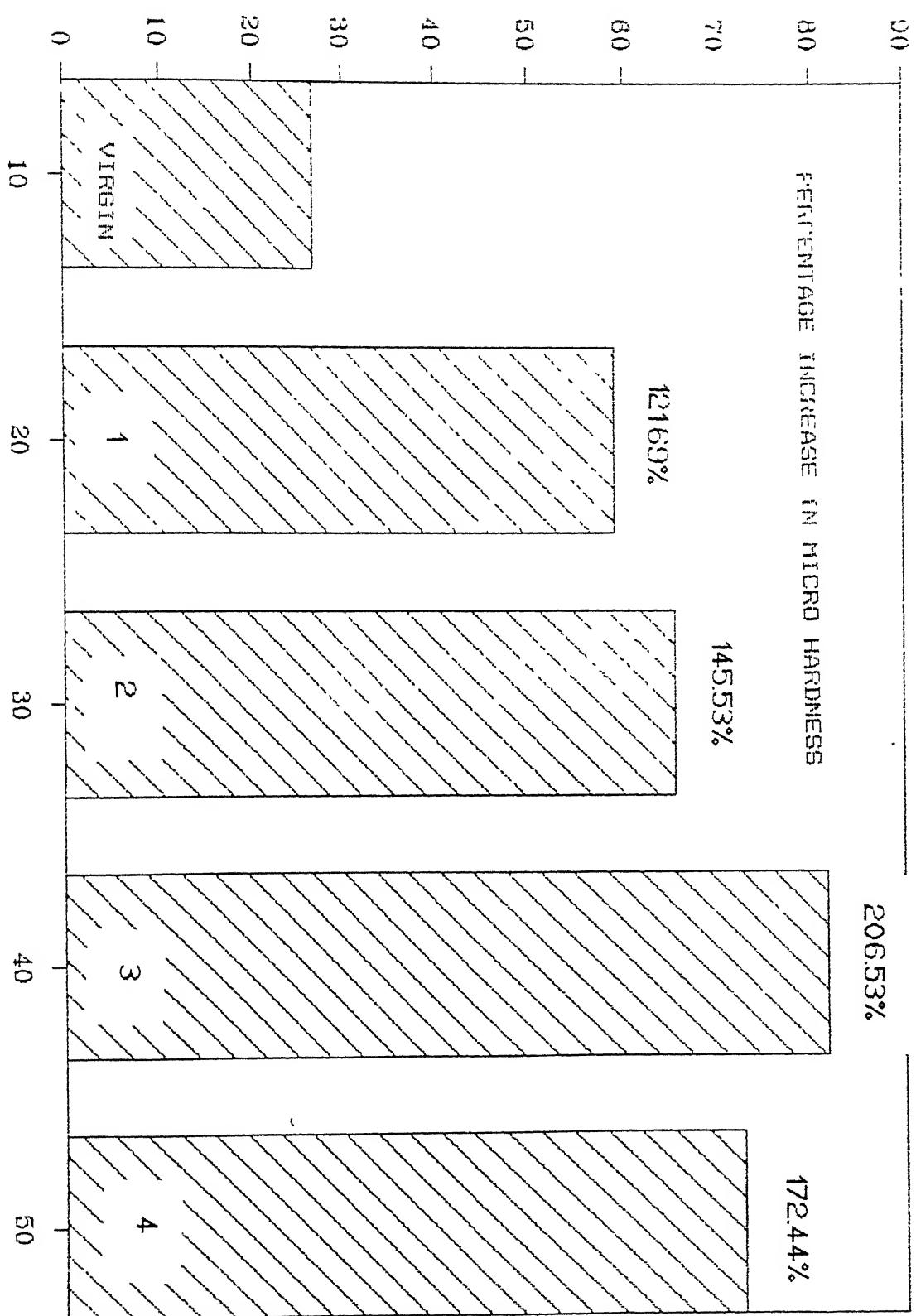


FIG. 3.7 DRYING CONDITION

MICROHARDNESS OF ANODIZED SAM.FOR 10min

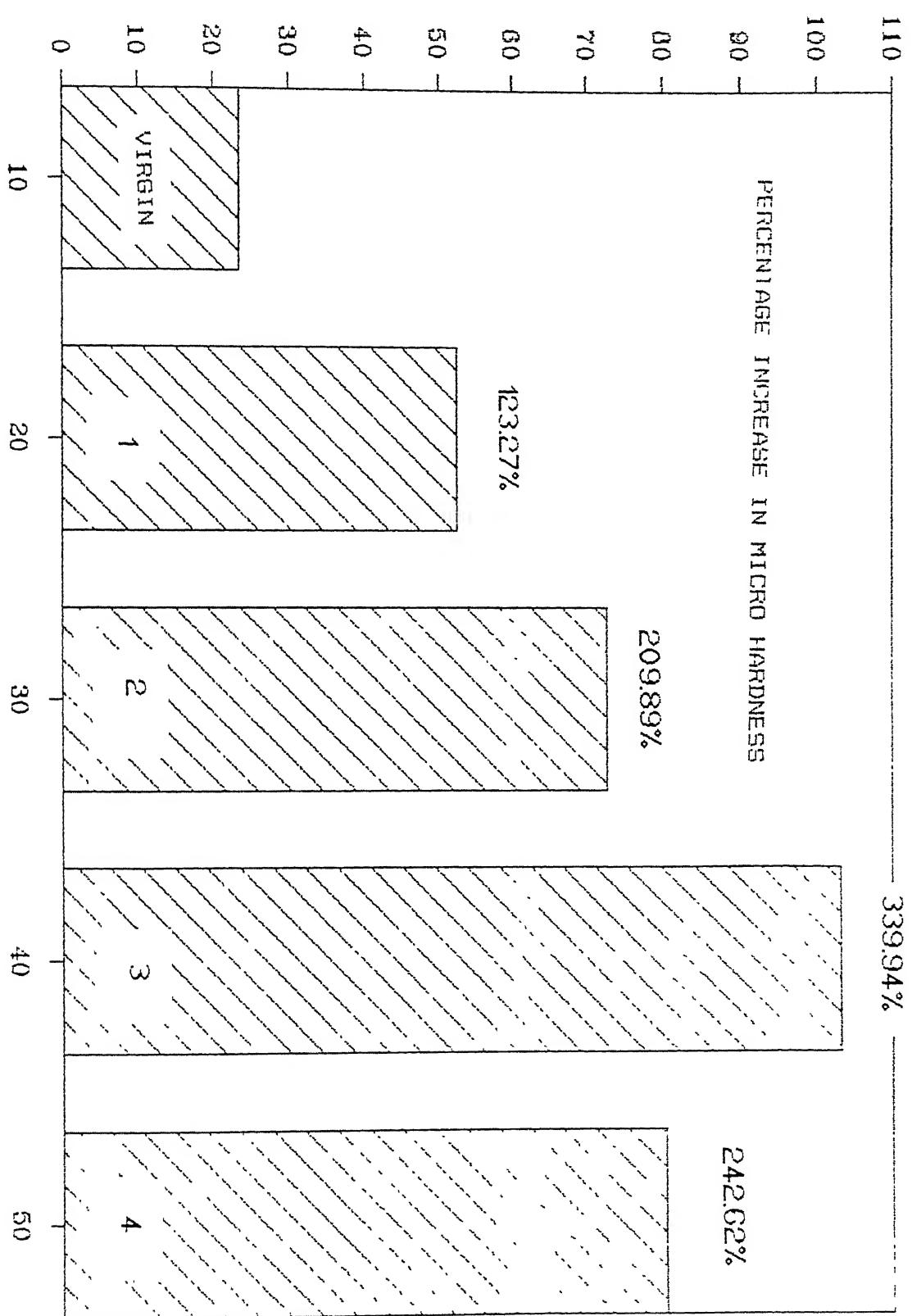


Fig 3.8 DRYING CONDITION

MICROHARDNESS OF ANODIZED SAM.FOR 15min

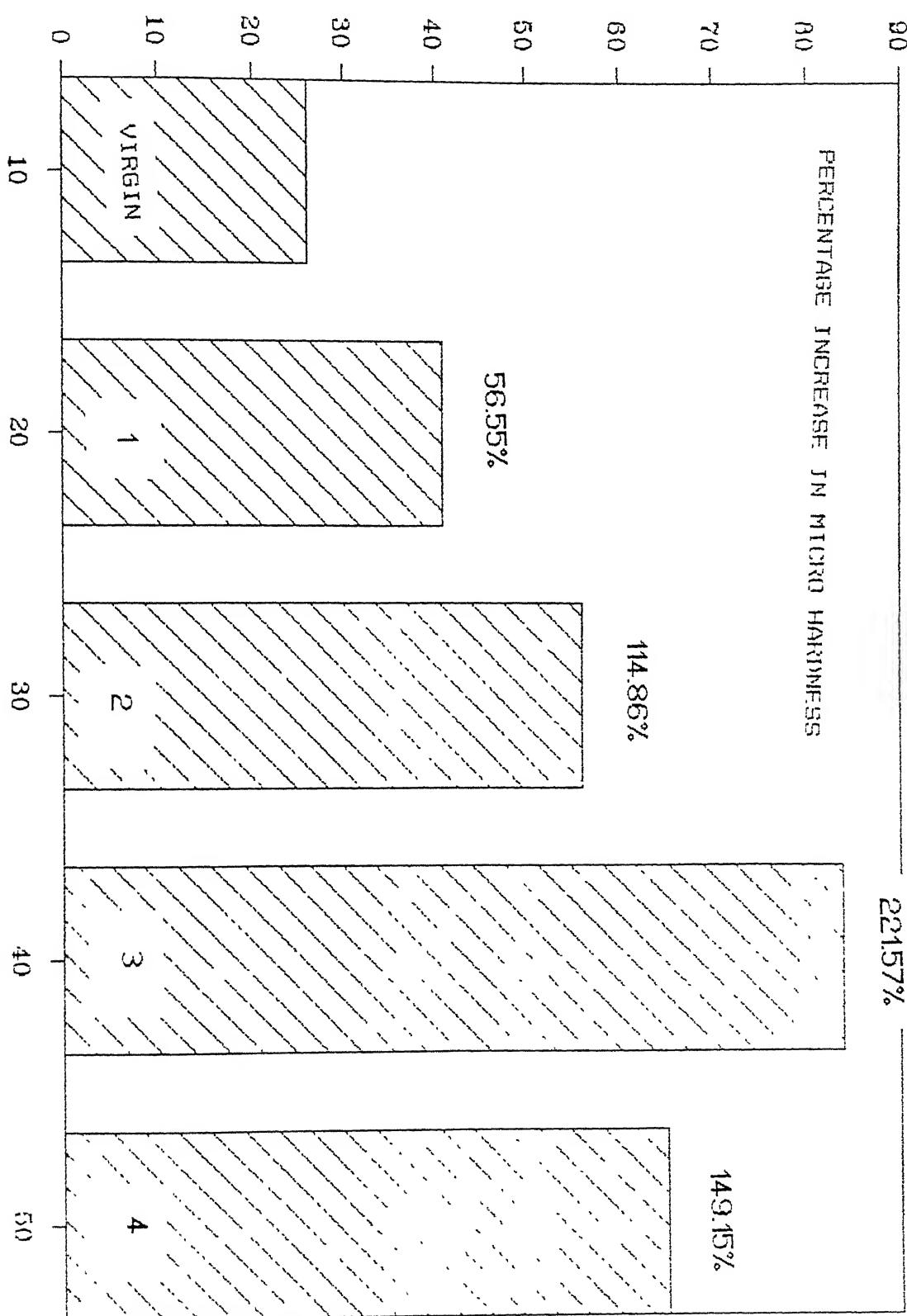


Fig 3.9 DRYING CONDITION

MICROHARDNESS OF ANODIZED SAM.FOR 20min

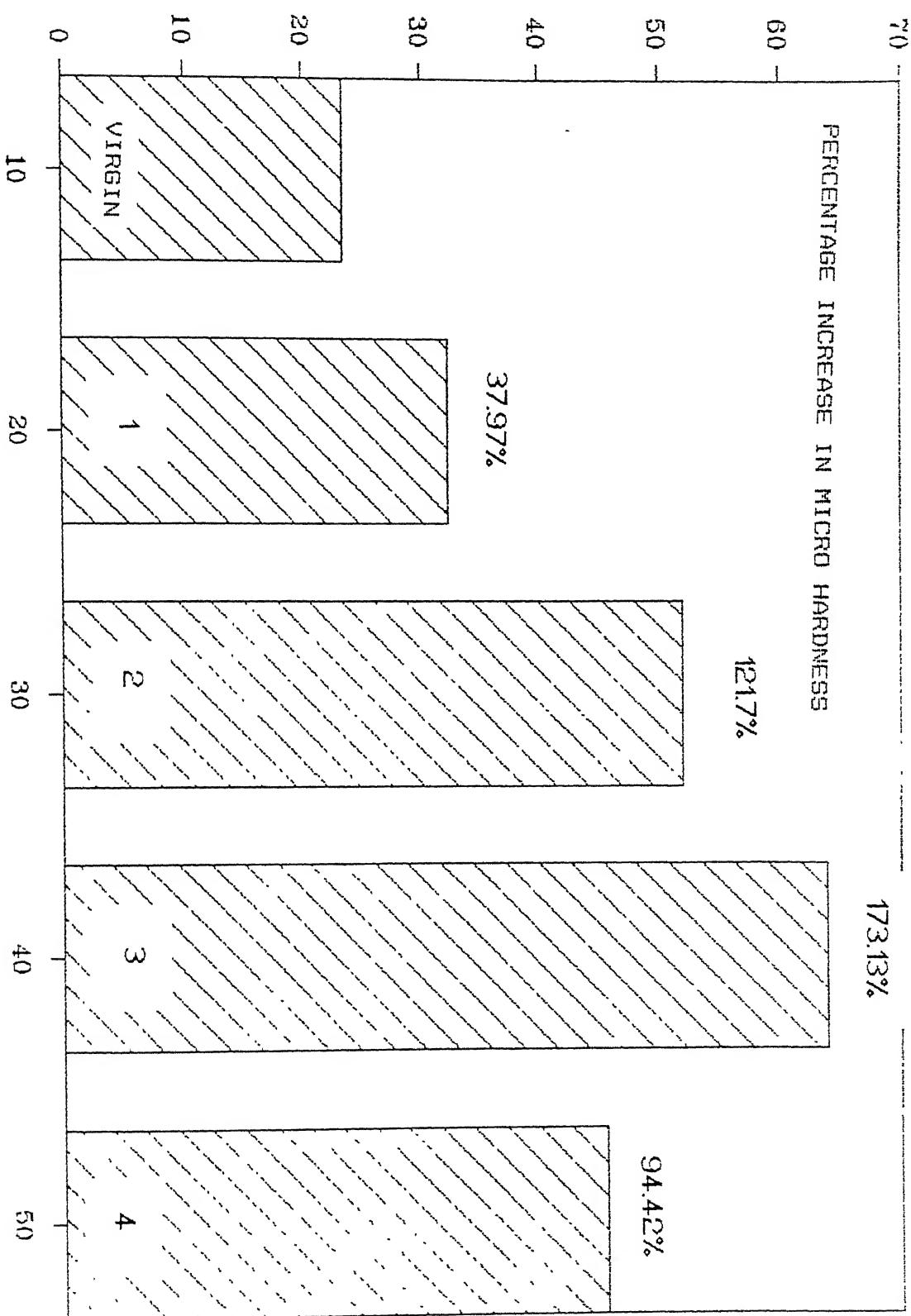


Fig.3.10 DRYING CONDITION

It is found that micro hardness of anodized coating increases with reference to virgin aluminium from  $23.46 \text{ kg/mm}^2$  to  $103.21 \text{ kg/mm}^2$  (for 10 minute anodization). Further it was noticed that increases in micro hardness value with anodizing time started deteriorating after anodizing time of 10 minutes and was attributed enhanced porosity in coating. Similar observations have been noted by Spooner et al.<sup>30,31</sup> The micro hardness of anodized sample was found to increases with storage time at room temperature ( $\sim 35^\circ\text{C}$ ) up to 48 hours. The heating of anodized coating to  $100^\circ\text{C}$  leads to significant increase from  $72.70 \text{ kg/mm}^2$  to  $103.21 \text{ kg/mm}^2$  (for 10 minutes anodization) micro hardness value (Table 3.15 & 3.16) However heating to  $200^\circ\text{C}$  induced significant decrease in hardness. These all has been sum up in Table 3.11, 3.18, 3.25, & 3.32 and depicted by bar charts in Fig.3.7, 3.8, 3.9, and 3.10. In bar chart 1, 2, 3, & 4 represents the sample conditions as mentioned in sum up table.

### 3.4 FLUORIDE ION ( $\text{F}^-$ ) ABSORPTION SYSTEM :

When water containing fluoride ion ( $\text{F}^-$ ) stored in a aluminium pot having anodic coating for some hours a significant amount of fluoride ion gets absorbed in the oxide coating. And due to that water gets purified.

The results of three different experiments has been tabulated below.

Fluoride ion (F<sup>-</sup>) absorbed in mg/l.

Duration (hrs.)	1	2	3
0.0	0.00	0.00	0.00
4.0	1.00	1.04	0.36
24.0	3.00	1.70	1.10
48.0	3.75	2.10	1.40

Percentage Active surface of fluoride ion (F<sup>-</sup>) m<sup>2</sup>/gm.

duration (hrs)	1	2	3	Average
0.0	0.00	0.00	0.00	0.00
4.0	26.60	49.52	26.13	34.08
24.0	80.00	80.96	78.57	79.84
48.0	100.00	100.00	100.00	100.00

Fig.3.11 Shows the plot of Active surface Vs duration.

Fig.3.12 Shows the plot of Percentage active surface Vs duration.

This behavior can be represented by an expression of type

$$\phi = At^n \quad \text{Where } n=0.5$$

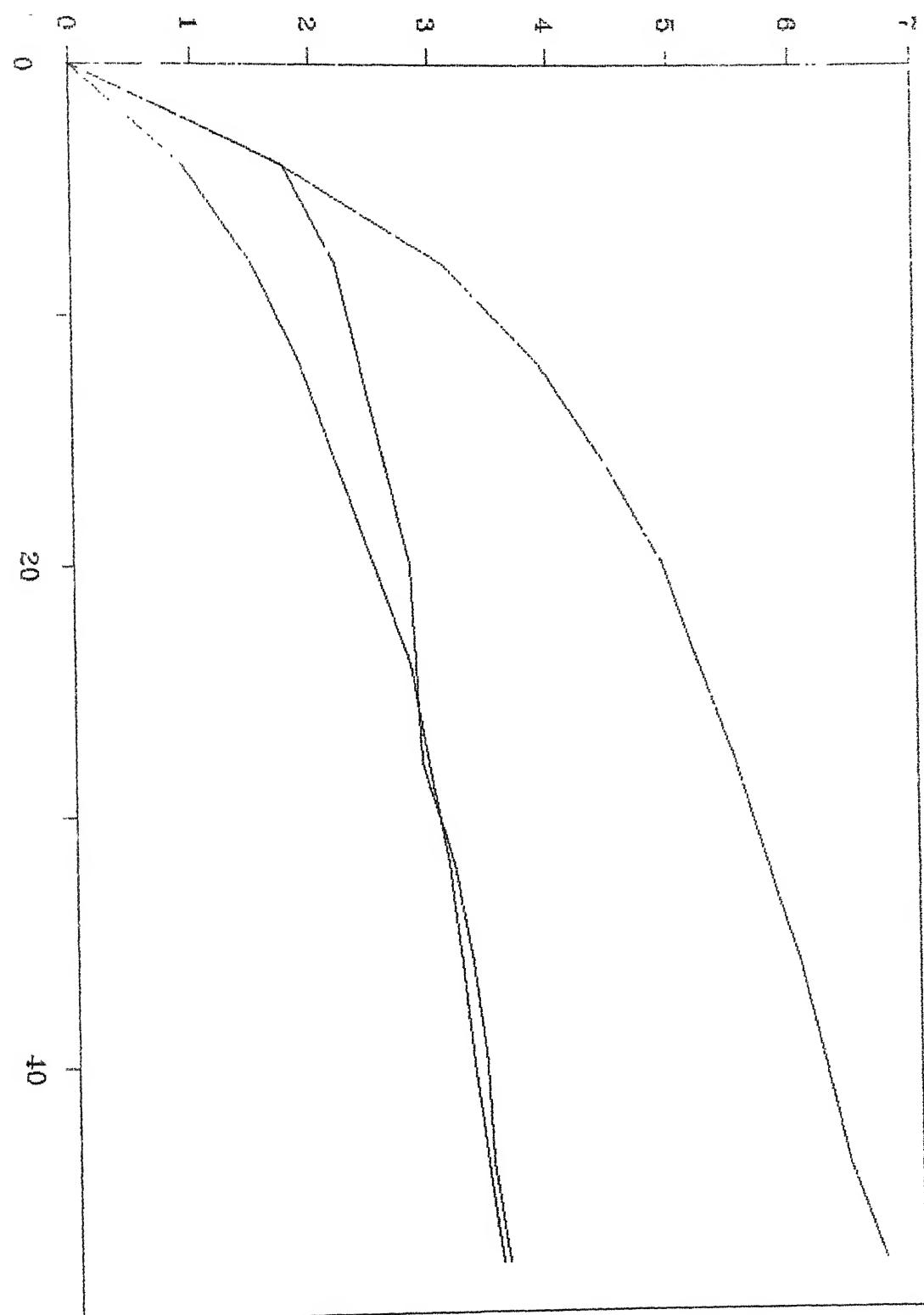
$$A=0.26081 \text{ if } t \text{ is in sec.}$$

$$=15.5 \quad \text{if } t \text{ is in hrs.}$$

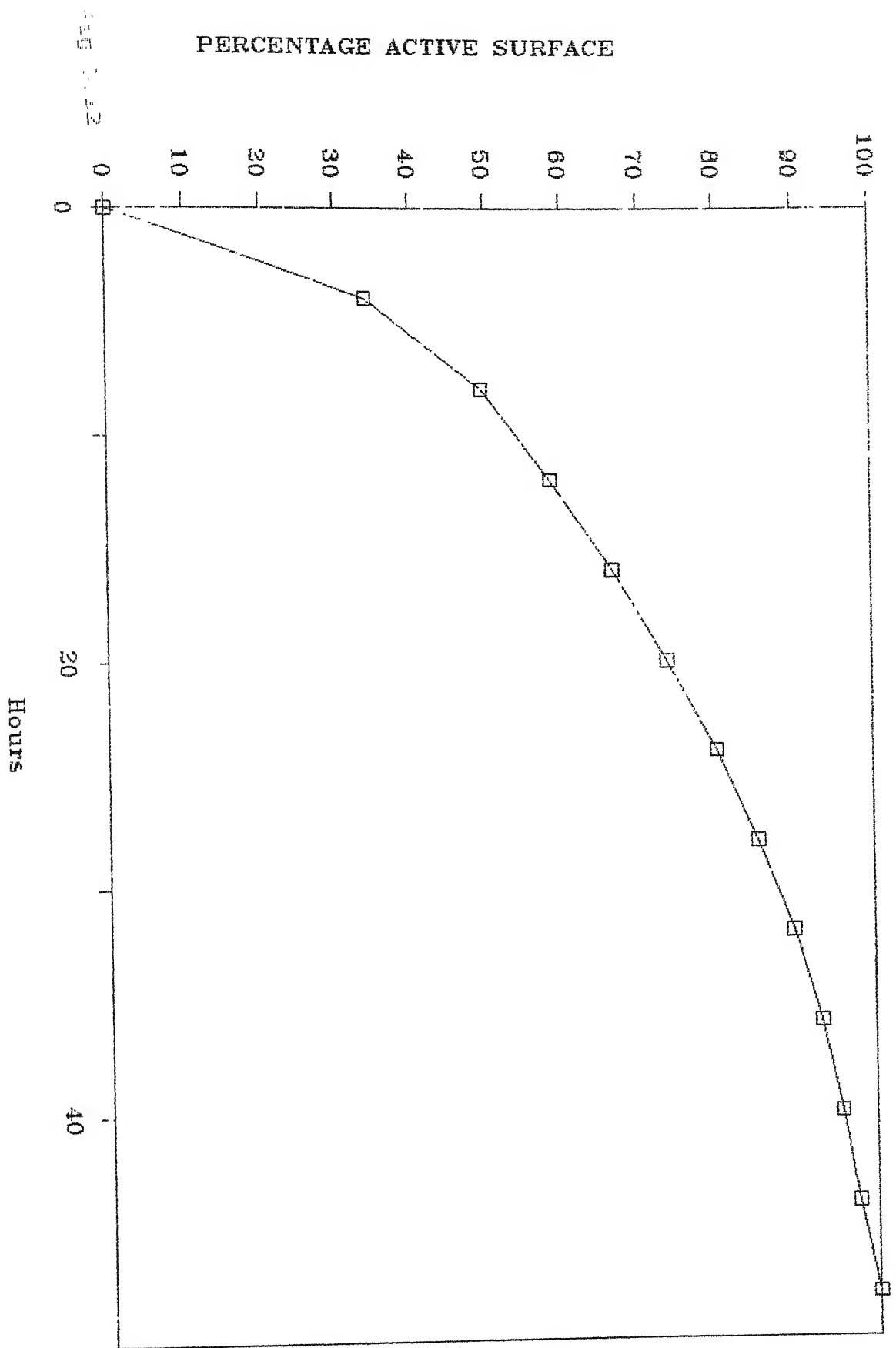
Same data also can be represented by fitted in a straight line of the type  $\phi^2 = Kt$ .

$$\text{Where } K=249 \text{ if } t \text{ is in hrs.}$$

ACTIVE SURFACE ( $m^2/gm$ )



PERCENTAGE ACTIVE SURFACE



## CONCLUSIONS AND SCOPE FOR FUTURE WORK

## 4.1 CONCLUSIONS

The major conclusion for the present study can be summarized as below:

- (i) The impurity elements in the aluminium sheet having more electropositive nature with respect to Aluminium have tendency to deplete.
- (ii) Anodized coating shows very high hardness in comparison to virgin aluminium.
- (iii) The micro hardness values increase up to limited extent with anodization time (up to ~ 10 minutes) and aging process.
- (iv) Finding (ii) and (iii) can be utilized in most likely hood to increase bear resistance of cast aluminium engine parts.
- (v) The anodic coating most probably hydrated aluminium oxide, was found to be active for  $F^-$  ion chemisorption. The process is slow and probably takes around 48 hours (two days) to saturate . The total active surface area of about  $3.514 \text{ m}^2/\text{gm}$  have been arrived. This shows a capacity of removing about 3.75 mg of  $F^-$  ions/liter of water over an area of  $208.5 \text{ cm}^2$  coated surface. This result is of great importance in designing water containers with abilities to extract out harmful fluoride ions from drinking water.

#### 4.2 SCOPE FOR FUTURE WORK

This works opens future possibility of studying abrasive resistance property of anodized aluminium surfaces in other electrolytes with respect to anodizing parameter such as electrolyte constitution, temperature, pH, anodizing current density, anodizing voltage and duration. Study on aging behavior of coating seems interesting specially with reference to thermal treatment.

It seems quite important to design and study anodizing aluminium reactor/water container with reference to abilities of  $F^-$  ion removal in more practical situation i.e. removing about 10 mg/l of  $F^-$  ions within an hour or so.

TABLE 3.1 Average of contents in virgin samples :-

Element	wt %	to 100%	Atom	K-ratio
Al	76.040	99.0998	99.4169	75.5452
Si	0.224	0.292	0.2814	0.1088
Cu	0.058	0.076	0.03228	0.0498
Mg	0.0138	0.0182	0.0525	0.0148
Fe	0.394	0.514	0.2491	0.352
Total	76.7298	100.00	100.00	76.0706

TABLE 3.2 Average of contents in samples anodized for 10 min.:-

Element	wt %	to 100%	Atom	K-ratio
Al	36.2244	98.9162	99.05326	36.1218
Si	0.3206	0.8754	0.842	0.1558
Cu	0.0322	0.0872	0.03716	0.0278
Mg	0.0038	0.0146	0.01606	0.0056
Fe	0.0392	0.1068	0.05156	0.0348
Total	36.6202	100.00	100.00	36.3458

TABLE 3.3 Relative depletion/enhancement of elements due to anodization with respect to virgin values

Element	Wt. Defference	Wt. Defference in %
Al	-39.8156	- 52.360
Si	0.0966	+ 43.152
Cu	-0.0258	- 44.48
Mg	-0.0100	- 72.46
Fe	-0.3548	+ 90.05
Total	36.6202 .	100.00

TABLE 3.4 Results of X-ray diffraction of anodized (10 min.) sample :-

(a) Due to anodized coating (Could not be indexed)

Peak No.	Plane (hkl)	$d_{hkl}$ (Exp.)	$I/I_0$	Peak Angle (Degree)
1.		6.05779	0.849	10.9
2.		4.63767	1.000	14.3
3.		4.27299	0.368	15.5
4.		4.05714	0.679	16.4

(b) Peaks from aluminium base after anodisation

Peak No.	Plane (hkl)	$d_{hkl}$ (Exp.)	$d_{hkl}$ (Theo.)	$I/I_0$	Peak Angle (Degree)
1.	111	2.33345	2.33826	1.000	29.4
2.	200	2.02240	2.02500	0.468	34.5
3.	220	1.42870	1.43189	0.316	53.3
4.	311	1.22057	1.22112	0.793	69.8

Source  $\text{CuK}_\alpha$

$a = 4.05 \text{ \AA}^\circ$

$\lambda = 2.291002 \text{ \AA}^\circ$

$$d_{hkl} (\text{Exp.}) = \frac{\lambda}{2 \sin \theta}$$

$$d_{hkl} (\text{Theo.}) = \frac{a}{(\sqrt{h^2 + k^2 + l^2})^{0.5}}$$

TABLE 3.5

## EXPERIMENTAL CONDITIONS

Anodization Time = 5 min.

Electrode separation = 17 mm.

Concentration of electrolyte = 0.16 M.

Volts (V)	Current (mA)	Temp. (° C)	Time Duration (min)
50 Constant	250	33.2	0
	380	38.9	1
	420	41.5	2
	430	43.0	3
	480	44.8	4
	490	44.5	5
Average	311.428	40.85	

Table 3.6 Micro hardness of virgin sample.

Weight = 50 gm.

Sl.No.	Hori. (μm)	Vert. (μm)	Avr. (μm)	H.V. (Kg./mm <sup>2</sup> )
1.	55.4	60.0	57.7	27.80
2.	58.5	59.0	58.75	26.85
3.	61.0	62.2	61.6	24.4
4.	59.0	58.6	58.8	26.8
5.	58.3	57.00	57.65	26.85
6.	60.0	59.10	59.55	26.15
Avr.			59.55	26.64

TABLE 3.7 Micro hardness of sample anodized for 5 min. (Dried for 11 hrs.).

Weight. = 100 gm.

Sl.No.	Hori. ( $\mu\text{m}$ )	Vert. ( $\mu\text{m}$ )	Avr. ( $\mu\text{m}$ )	H.V. ( $\text{Kg./mm}^2$ )
1.	54.3	52.0	53.15	65.40
2.	52.5	53.2	52.85	66.40
3.	58.6	56.00	57.30	56.50
4.	56.50	55.90	56.20	58.70
5.	59.20	58.70	57.95	53.35
6.	57.90	59.30	58.60	54.00
Avr.			56.17	59.06

TABLE 3.8 Micro hardness of sample anodized for 5 min. (Dried for 27 hrs.).

Weight = 100 gm.

Sl.No.	Hori. ( $\mu\text{m}$ )	Vert. ( $\mu\text{m}$ )	Avr. ( $\mu\text{m}$ )	H.V. ( $\text{Kg./mm}^2$ )
1.	56.7	52.20	54.60	62.20
2.	53.6	56.00	54.80	61.70
3.	55.20	57.20	56.20	58.70
4.	53.40	47.20	50.30	73.30
5.	53.20	50.40	51.80	69.10
6.	53.40	51.40	52.40	67.50
Avr.			53.35	65.41

TABLE 3.9 Micro hardness of sample anodized for 5 min. (Heated for 2 hrs. at 100 °C and furnace cooled).

Weight = 100 gm.

Sl.No.	Hori. (μm)	Vert. (μm)	Avr. (μm)	H.V. (Kg./mm <sup>2</sup> )
1.	50.60	48.00	49.30	76.30
2.	46.30	49.50	47.90	80.80
3.	48.40	50.00	49.20	76.60
4.	49.40	44.80	47.10	83.60
5.	46.80	47.00	46.90	84.30
6.	46.30	45.30	45.80	88.40
Avr.			47.70	81.66

TABLE 3.10 Micro hardness of sample anodized for 5 min. (heated at 200°C for 3 hrs. and furnace cooled).

Weight = 100 gm.

Sl.No.	Hori. (μm)	Vert. (μm)	Avr. (μm)	H.V. (Kg./mm <sup>2</sup> )
1.	50.20	52.40	51.30	70.50
2.	49.30	50.30	49.80	74.80
3.	50.90	47.50	49.20	76.60
4.	48.40	52.40	50.40	73.00
5.	54.70	51.70	53.20	65.50
6.	51.10	48.30	49.70	75.10
Avr.			50.60	72.58

TABLE 3.11 Percentage increase in micro hardness of samples anodized for 5 min.

Sr No	Sample condition	m.h. (processed)	% increase in m.h.
		m.h. (virgin)	
1.	Dried for 11 hrs after anodization	2.21	121.69
2.	Dried for 47 hrs after anodization	2.45	145.53
3.	Heat at 100 °C for 2 hrs. and furnace cooled	3.06	206.53
4.	Heated at 200 °C for 3 hrs and furnace cooled	2.72	172.44

TABLE 3.12

## EXPERIMENTAL CONDITIONS

Anodization Time = 10 min.

Electrode separation = 17 mm.

Concentration of electrolyte = 0.16 M

Volts (V)	Current (mA)	Temp. (° C)	Time Duration (min)
50 Constant	450	33.00	0
	500	35.00	1
	550	38.20	2
	600	41.90	3
	620	45.00	4
	640	47.50	5
	650	50.20	6
	660	53.00	7
	664	55.20	8
	660	57.00	9
	655	58.90	10
Average	604.45	46.80	

Table 3.13 Micro hardness of virgin sample.

Weight = 50 gm.

Sl.No.	Hori. ( $\mu\text{m}$ )	Vert. ( $\mu\text{m}$ )	Avr. ( $\mu\text{m}$ )	H.V. ( $\text{Kg./mm}^2$ )
1.	60.00	61.00	60.50	25.30
2.	61.50	64.50	63.00	23.40
3.	68.00	67.00	67.50	20.40
4.	64.00	65.40	64.70	22.10
5.	60.00	60.00	60.00	25.80
6.	63.80	61.00	62.40	23.80
Avr.			63.02	23.46

TABLE 3.14 Micro hardness of sample anodized for 10 min. (Dried for 3 hrs.).

Weight. = 100 gm.

Sl.No.	Hori. ( $\mu\text{m}$ )	Vert. ( $\mu\text{m}$ )	Avr. ( $\mu\text{m}$ )	H.V. ( $\text{Kg./mm}^2$ )
1.	59.60	64.00	61.80	48.50
2.	61.50	60.30	60.90	50.00
3.	61.40	61.20	61.30	59.30
4.	60.60	59.00	59.80	51.80
5.	58.60	61.60	60.10	51.30
6.	60.80	57.00	58.90	53.40
Avr.			60.46	52.38

TABLE 3.15 Micro hardness of sample anodized for 10 min.  
(Dried for 45 hrs).

Weight = 100 gm.

Sl.No.	Hori. ( $\mu\text{m}$ )	Vert. ( $\mu\text{m}$ )	Avr. ( $\mu\text{m}$ )	H.V. ( $\text{Kg.}/\text{mm}^2$ )
1.	49.40	51.50	50.45	72.85
2.	48.50	51.40	49.95	74.35
3.	50.80	54.60	52.70	66.80
4.	53.40	49.50	51.45	70.20
5.	50.40	46.00	48.20	79.80
6.	52.80	48.50	50.65	72.25
Avr.			50.56	72.70

TABLE 3.16 Micro hardness of sample anodized for 10min. (Heated for 2 hrs. at  $100^\circ\text{C}$  and furnace cooled).

Weight = 100 gm.

Sl.No.	Hori. ( $\mu\text{m}$ )	Vert. ( $\mu\text{m}$ )	Avr. ( $\mu\text{m}$ )	H.V. ( $\text{Kg.}/\text{mm}^2$ )
1.	39.10	45.50	42.30	103.00
2.	40.10	40.00	40.05	115.50
3.	42.50	43.40	42.95	100.50
4.	46.10	46.60	46.35	86.30
5.	40.00	43.00	41.50	108.00
6.	41.20	42.40	41.80	106.00
Avr.			42.49	103.21

TABLE 3.17 Micro hardness of sample anodized for 10 min. (heated at 200 °C for 3 hrs. and furnace cooled).  
Weight = 100 gm.

Sl.No.	Hori. (μm)	Vert. (μm)	Avr. (μm)	H.V. (Kg./mm <sup>2</sup> )
1.	48.50	43.00	45.75	88.60
2.	48.00	47.20	47.60	81.80
3.	49.30	50.80	50.05	74.50
4.	47.60	49.30	48.50	78.80
5.	48.80	48.20	48.50	78.80
6.	47.90	49.70	48.20	79.80
Avr.			48.10	80.38

TABLE 3.18 Percentage increase in micro hardness of samples anodized for 10 min.

Sr No	Sample condition	m.h. (processed)	% increase in m.h.
		m.h. (virgin)	
1.	Dried for 11 hrs after anodization	2.2327	123.27
2.	Dried for 47 hrs after anodization	3.0989	209.89
3.	Heat at 100 °C for 2 hrs. and furnace cooled	4.3994	339.94
4.	Heated at 200 °C for 3 hrs and furnace cooled	3.4262	242.62

TABLE 3.19

## EXPERIMENTAL CONDITIONS

Anodization Time = 15 min.,      Electrode separation = 17 mm.

Concentration of electrolyte = 0.16 M.

Volts (V)	Current (mA)	Temp. (°C)	Time Duration (min)
50 Constant	260	31.90	0
	410	33.20	1
	445	35.00	2
	490	37.00	3
	510	39.00	4
	540	42.00	5
	550	46.00	6
	560	49.20	7
	565	50.50	8
	570	52.60	9
	575	55.70	10
	580	57.00	11
	570	58.00	12
	560	59.50	13
	550	60.00	14
	545	61.00	15
Avrg.	517.50	47.97	

Table 3.20 Micro hardness of virgin sample.

Weight = 50 gm.

Sl.No.	Hori. ( $\mu\text{m}$ )	Vert. ( $\mu\text{m}$ )	Avr. ( $\mu\text{m}$ )	H.V. ( $\text{Kg./mm}^2$ )
1.	60.30	58.50	59.40	26.30
2.	63.20	61.10	62.15	24.00
3.	61.00	61.50	61.25	24.75
4.	60.70	60.90	60.80	25.10
5.	54.90	55.50	55.20	30.40
6.	60.30	58.90	59.60	26.10
Avr.			59.73	26.10

TABLE 3.21 Micro hardness of sample anodized for 15min. (Dried for 4 hrs.).

Weight.= 100 gm.

Sl.No.	Hori. ( $\mu\text{m}$ )	Vert. ( $\mu\text{m}$ )	Avr. ( $\mu\text{m}$ )	H.V. ( $\text{Kg./mm}^2$ )
1.	65.90	66.70	66.30	42.20
2.	68.70	67.50	68.10	40.00
3.	68.10	66.90	67.50	40.70
4.	65.80	68.00	66.90	41.40
5.	66.70	67.50	67.10	41.20
6.	67.10	69.50	68.30	39.70
Avr.			67.36	40.86

TABLE 3.22 Micro hardness of sample anodized for 15min. (Dried for 46 hrs). Weight = 100 gm.

Sl.No.	Hori. ( $\mu\text{m}$ )	Vert. ( $\mu\text{m}$ )	Avr. ( $\mu\text{m}$ )	H.V. ( $\text{Kg./mm}^2$ )
1.	56.90	59.70	58.30	54.5
2.	60.30	59.10	59.70	52.0
3.	57.50	56.30	56.90	57.3
4.	56.70	54.90	55.80	59.5
5.	56.10	58.70	57.40	56.3
6.	56.40	57.80	57.10	56.9
Avr.			57.53	56.08

TABLE 3.23 Micro hardness of sample anodized for 15 min. (Heated for 2 hrs. at  $100^\circ\text{C}$  and furnace cooled).

Weight = 100 gm.

Sl.No.	Hori. ( $\mu\text{m}$ )	Vert. ( $\mu\text{m}$ )	Avr. ( $\mu\text{m}$ )	H.V. ( $\text{Kg./mm}^2$ )
1.	48.30	45.90	47.10	83.60
2.	46.10	46.50	46.30	86.50
3.	47.90	49.10	48.50	78.80
4.	47.80	48.40	48.10	80.20
5.	46.10	45.70	45.90	88.00
6.	46.20	46.40	48.30	86.50
Avr.			47.03	83.93

TABLE 3.24 Micro hardness of sample anodized for 15 min. (heated at 200 °C for 3 hrs. and furnace cooled).

Weight = 100 gm.

Sl.No.	Hori. (μm)	Vert. (μm)	Avr. (μm)	H.V. (Kg./mm <sup>2</sup> )
1.	52.70	53.70	53.20	65.50
2.	53.10	55.10	54.10	63.30
3.	54.30	52.90	53.60	64.30
4.	53.20	52.60	52.90	66.30
5.	53.60	53.80	53.70	64.30
6.	52.50	53.10	52.80	66.50
Avr.			53.38	65.03

TABLE 3.25 Percentage increase in micro hardness of samples anodized for 15 min.

Sr No	Sample condition	m.h. (processed)	% increase in m.h.
		m.h. (virgin)	
1.	Dried for 4 hrs after anodization	1.5655	56.55
2.	Dried for 46 hrs after anodization	2.1486	114.86
3.	Heat at 100 °C for 2 hrs. and furnace cooled	3.2157	221.57
4.	Heated at 200 °C for 3 hrs and furnace cooled	2.4915	149.15

TABLE 3.26

## EXPERIMENTAL CONDITIONS

Anodization Time = 20 min.

Electrode separation = 17 mm.

Concentration of electrolyte = 0.16 M.

Volts (V)	Current (mA)	Temp. (°C)	Time Duration (min)
50 Constant	250	32.00	0
	400	35.00	1
	450	37.00	2
	500	39.20	3
	530	42.50	4
	545	45.20	5
	556	47.70	6
	560	50.00	7
	564	52.00	8
	564	54.00	9
	570	55.20	10
	590	57.20	11
	580	58.80	12
	560	60.00	13
	550	60.50	14
	550	61.20	15
	545	62.00	16

	540	62.90	17
	535	63.50	18
	530	64.50	19
	520	65.50	20
Average	545.14	52.66	

TABLE 3.27 Micro hardness of virgin sample.

Weight =50 gm.

Sl.No.	Hori. ( $\mu\text{m}$ )	Vert. ( $\mu\text{m}$ )	Avr. ( $\mu\text{m}$ )	H.V. ( $\text{Kg.}/\text{mm}^2$ )
1.	63.00	67.00	65.00	21.90
2.	64.20	60.00	62.10	24.00
3.	66.70	60.00	63.35	23.10
4.	63.30	60.00	61.65	24.40
5.	63.00	61.50	62.25	23.95
6.	66.50	60.00	63.25	23.15
Avr.			62.93	23.40

TABLE 3.28. Micro hardness of sample anodized for 20min. ( Dried for 3 hrs.).

Weight. = 100 gm.

Sl.No.	Horiz. (μm)	Vert. (μm)	Avr. (μm)	H.V. (Kg./mm <sup>2</sup> )
1.	36.00	73.90	76.95	31.35
2.	77.00	78.50	77.75	30.65
3.	77.40	81.00	78.70	31.50
4.	77.40	72.70	75.05	32.95
5.	76.50	69.00	72.75	35.05
Avrs.			75.84	32.30

TABLE 3.29 Micro hardness of sample anodized for 20 min. (Dried for 48 hrs.). Weight = 100 gm.

Sl.No.	Horiz. (μm)	Vert. (μm)	Avr. (μm)	H.V. (Kg./mm <sup>2</sup> )
1.	54.00	57.00	55.50	60.20
2.	50.50	64.40	62.45	47.55
3.	54.10	58.20	56.15	58.80
4.	63.20	60.50	61.85	48.45
5.	60.50	60.10	60.30	51.00
6.	65.30	62.50	63.90	45.40
Avrs.			60.02	51.90

TABLE 3.30 Micro hardness of sample anodized for 20 min. (Heated for 2 hrs. at 100 °C and furnace cooled).

Weight = 100 gm.

Sl. No	Hori. (μm)	Vert. (μm)	Avr. (μm)	H.V. (Kg./mm <sup>2</sup> )
1	56.00	57.20	56.60	57.90
2	54.20	55.00	54.60	62.00
3	51.80	51.70	51.75	69.25
4	55.10	54.20	54.65	62.10
5	52.80	54.10	53.45	64.90
6	51.40	53.40	52.40	67.50
Avr.			53.91	63.94

TABLE 3.31 Micro hardness of sample anodized for 20 min (heated at 200 °C for 3 hrs. and furnace cooled).

Weight = 100 gm.

Sl. No.	Hori. (μm)	Vert. (μm)	Avr. (μm)	H.V. (Kg./mm <sup>2</sup> )
1.	59.00	57.50	58.25	54.60
2.	67.40	60.00	63.70	45.70
3.	65.40	63.20	64.30	44.80
4.	62.30	64.60	63.45	46.50
5.	66.20	64.70	65.45	43.25
6.	69.30	70.00	69.65	38.25

Avr.		64.13	45.51
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TABLE 3.32 Percentage increase in micro hardness of samples anodized for 20 min.

Sr. no	Sample condition	m.h. (processed)	% increase in m.h.
		m.h. (virgin)	
1.	Oxidized for 3 hrs after anodization	1.3797	37.97
2.	Oxidized for 48 hrs after anodization	2.2170	121.70
3.	Heat at 100 °C for 2 hrs. and furnace cooled	2.7313	173.13
4.	Heated at 200 °C for 3 hrs and furnace cooled	1.9442	94.42

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